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This report describes the findings of an investigation on the sources and treatment of industrial wastewater containing metals. The study was performed to assess the existing database on metal containing wastewaters, investigate the state of development on the various treatment technologies being used, and determine whether this information could be applied to water treatment problems in the nonferrous metals industry. The results are being used within the Agency's Office of Research and Development as part of a larger effort to define potential environmental impact of emissions and effluents from this industry and the need for improved controls. The findings will also be useful to other Agency components and the industry in dealing with environmental control problems. The Metals and Inorganic Chemicals Branch of the Industrial Pollution Control Division should be contacted for additional information desired concerning this program.

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SOURCES AND TREATMENT OF WASTEWATER IN THE NONFERROUS METALS INDUSTRY

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report presents the findings of an investigation of the sources and treatment of industrial wastewater which contains metals. The study was performed to assess the existing data base on metal containing wastewaters, investigate the state of development of the various treatment technologies being used, and determine whether this information could be applied to the water treatment problems in the nonferrous metals industry. The results are being used within the Agency's Office of Research and Development as part of a larger effort to define the potential environmental impact of emissions from this industry and the need for improved controls. The findings will also be useful to other Agency components and the industry in dealing with environmental control problems. The Metals and Inorganic Chemicals Branch of the Industrial Pollution Control Division should be contacted for any additional information desired concerning this program.

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ABSTRACT

In this report, the available literature data were compiled on both the sources of and treatment technologies for industrial acidic wastewater containing dissolved heavy metals. The intent was to assess the applicability of existing wastewater treatment technology to the effluents generated by the primary and secondary copper, lead, and zinc industries.

A list of industries and processes they employ which discharge acidic wastewater containing metals was compiled by reviewing available literature. A list of available treatment technologies was compiled both from the literature and from industrial vendors and users. In addition, the wastewater sources and treatment technologies in the nonferrous metals industry were investigated.

Each treatment technology of interest was evaluated based on:

- control effectiveness for heavy metals in water,
- energy requirements,
- economics, and
- secondary process emissions.

As a result of these evaluations, two wastewater treatment processes, hydroxide precipitation and evaporation were found to be widely used commercially and applicable to the treatment of effluents in the nonferrous metals industry. The applicability of evaporation is limited to arid regions.

Two other processes, sulfide precipitation and ferrite coprecipitation, have been successfully used in limited applications in Sweden and Japan to treat metal containing wastewater. These processes appear to be particularly applicable to the primary nonferrous metals industry because the solid waste that is generated can be recycled to a smelting furnace.

The sodium borohydride reduction process may be useful for small wastewater streams containing either valuable or hard to remove metals, e.g., mercury and selenium. However, this process is not likely to be used on large volume, low metal concentration wastewaters.

Starch complexing has been applied in pilot studies as a polishing process. Good removal efficiencies are reported. However, the solid waste that is generated when absorbed compounds are released upon

decomposition of the starch results in a concentrated stream which must be treated by other means. Additional testing is required to determine if this process is applicable to commercial-scale wastewater treatment problems.

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SECTION 1

INTRODUCTION

Industrial effluent waters containing dissolved heavy metals represent an environmental problem associated with the activities of many industries. Important sources of such discharges range from metal treatment operations associated with the automotive industry to smelting and refining of basic materials such as copper, lead, and zinc. Different control techniques have been used or studied, both in the United States and abroad, for the many types of discharges which are involved. Unfortunately there has to date been no coordinated attempt to determine how applicable technology being studied or used abroad may be to wastewater problems in the United States. It is known however, that present control practices are especially limited for streams containing a number of specific metals such as mercury, selenium, and hexavalent chromium (Cr^{+6}).

The Industrial Environmental Research Laboratory (IERL) in Cincinnati is responsible for developing control technology for a number of industries producing wastewater containing dissolved heavy metals. One of the sources of such discharges within their areas of responsibility is the primary nonferrous metal industries. Discharges from these industries present some of the most difficult treatment problems. It is the purpose of this study to:

- identify significant sources of industrial wastewaters containing metal,
- assess the technologies being employed for treating wastewaters containing metal, and
- evaluate industry's control of the nonferrous metals discharges.

SECTION 2

PROJECT OVERVIEW

A literature search was performed with special attention to reports from past industry studies by EPA dealing with acidic wastewater sources. Acidic wastewaters are of particular interest because of the relatively high solubility of most metals in acidic solutions as compared to basic solutions. A list of industries and the processes they employ which discharge waters contaminated by dissolved heavy metals was then developed and characterized as completely as possible from available literature.

In a second step, centers of experience and expertise in dealing with treatment of metal containing wastewaters were identified and a list of technologies being employed by different industries was developed. Information from the literature was supplemented with background data from selected vendors and users of wastewater treatment technology. A list of technologies was developed to show their stage of development and their industrial applications.

Concurrent with the discharge assessment and control technology investigation, a study was carried out to define discharges of interest from the nonferrous metal industries. The data accumulated were used to identify specific control methods worthy of further evaluation for treatment of discharges from the production of nonferrous metals.

After treatment methods were identified, a process description was developed and the methods of interest were evaluated from the standpoint of:

- their removal effectiveness for metals in water, individually or collectively, where a number of heavy metals are present,
- the cost which might be associated with their application to discharges from the nonferrous metal industries,
- their energy requirements, and
- secondary discharges which they might produce.

After completion of the treatment technology assessment, problems that limit their applicability to the nonferrous metals industry were identified and approaches to developing solutions for these problems were recommended.

SECTION 3

RESULTS

In this section, the data on the sources and treatment of acidic wastewater are summarized. These data were gathered from both industry contacts and the open literature. Information about the following areas is presented:

- Sources of acidic wastewater containing metals,
- Available wastewater treatment methods
  - control effectiveness
  - energy requirements
  - economics
  - secondary process emissions, and
- Wastewater sources in the nonferrous metals industry.

SOURCES OF INDUSTRIAL ACIDIC WASTEWATER

The broad survey of available literature on sources and treatment of acidic wastewater was done to insure that a complete list of available treatment technologies was developed. The results of this survey indicate that the major sources of industrial acidic wastewater (pH <7.0) containing metals are:

- inorganic chemicals industry,
- organic chemicals industry,
- tire manufacturing,
- paint and ink production,
- electronics industry,
- iron and steel industry,
- metal fabrication and finishing,
- textile manufacturing,
- mining industries,
- photographic industry, and
- steam generation.

The elements most frequently found in discharge streams are:

aluminum
silver
arsenic
chromium
copper
iron
mercury
lead
nickel
selenium
tin
cadmium
manganese
zinc

Concentration ranges reported are shown in Table 1. Each of these sources is described in more detail in Section 5 and the report Appendix.

Hydroxide precipitation was found to be the most commonly used wastewater treatment technology in use. However, the data available in the open literature did not provide a comprehensive picture of the character of industrial wastewater. Rather, as indicated in Table 1 and the report Appendix, the data are sparse, especially with respect to removal efficiencies for different treatment technologies. As a result, there was little information which was suitable for comparison with the data available on nonferrous metal industry wastewaters and their treatment.

WASTEWATER TREATMENT TECHNOLOGY

A summary of available treatment methods is presented in Table 2. The important result shown in this table is that only two processes, hydroxide precipitation and evaporation ponds, are both commercially available and potentially applicable to the nonferrous metals industry. The applicability of evaporation, of course, is limited to arid regions.

Two other processes, sulfide precipitation and ferrite coprecipitation, have been successfully used in limited applications to treat wastewater containing metals. These processes appear to be particularly applicable to the primary nonferrous metals industry because the solid waste generated can be recycled to a smelting furnace. The sulfide process has been used to treat smelter wastewaters at the Boliden Metall copper smelter in Sweden and the Furukawa Co. Ltd.'s copper smelter in Japan.

The sodium borohydride reduction process may be useful for small wastewater streams containing either valuable or hard to remove metals, e.g., mercury and selenium. However, this process is not likely to be used on large volume, low metal concentration wastewaters.

Starch complexing has been applied in pilot studies as a polishing process. Good removal efficiencies are reported. However, disposal of the solid waste that is generated when the absorbed compounds are released upon decomposition of the starch results in a concentrated stream which must be treated by other means. Additional testing is required to determine the applicability of this process to commercial-scale wastewater treatment problems.

Both the reverse osmosis and ion exchange processes produce secondary effluents requiring further treatment. In addition, the pretreatment which would be required for smelter wastewaters would reduce their potential cost effectiveness. Activated carbon is primarily useful for removing organics from wastewater. It is unlikely that this process would be designed specifically to remove metals from a wastewater stream.

The following discussion presents the data collected concerning control effectiveness, energy requirements, economics, and secondary effluents on the nine treatment processes mentioned above. A summary of this data is shown in Table 3.

TABLE 1. SOURCES OF WASTEWATER CONTAINING HEAVY METALS

		Nature of Discharge mg/ℓ													
Industry	Process/Unit Operation	Al	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Se	Sn	Zn
Inorganic Chemicals	Chloralkali								18						
	Pigment					.5-95					0-12				19.5
	Acids			200-500	P										
	Basic Chemicals					0.1-0.5	0.1-1	40-250			0.2-0.7				
	Fertilizers			P	P					P					
Organic Chemicals	Petrochemicals, Polymers, Basic Chemicals	P		P	P	.04-4.6	.1-288	.4-500	P		66-145			P	0.1-3
Tire Manufacturing	Cooling Tower Blowdown					.1									.1
Paint & Ink	Miscellaneous Process Operations	29		P		.08	.04-.4	3-139		P	.4-5				3-77
Electronics	Batteries									P	.4-66				
	TV Tube Manufacturing										400				
Iron & Steel	Pickling, Plating, Galvanizing	P				.6-85	P	4-800	P	P	.5-1.4			61	2-880
	Spent Acid Pickling Solution							80,000							
Metal Fabrication & Finishing	Plating Drag Out		50-250		7-240	1-100	0-900	0-60			0-2	0-900			0-220
	Plating Bath Drums		13,000-45,000		2,000-23,000	10,000-270,000					140				5,000-34,000
	Others				14-22		4-880	60				3			
Explosives Industry	Lead Azide & Styphnate										0-200				
Textiles	Dyes, Rayon, Mills, Vulcanized Fiber					P	P	P							20-1,000
Mining Industries	Copper						.1-900				.1-3	.1-3			.1-3
	Lead & Zinc				0-1,000				.1	.02-57	.1-5				.03-38
	Iron: Mine Discharge								.002-2	.001-18	.001-.1				.0001-8
	Iron: Raw Mill Wastewater							.2-10		.01-20	.1-5				.01-10
	Silver							.3-2		.4-6					
	Bauxite	6-9													.4-2.
	Ferroalloy Ores				.2-.7		20-50	1,300-1,500		.2-56	2-10				25-77
	Coal: Mine Wastewater	.01-270	-	-	-	-	-	40-330	-	.01-127	-	.01-6	-	-	.01-13
	Coal: Acid Mine Drainage	.1-83		22	.02-1		.2-128	20-800		4-14	0-3	0.5-3			7-294
Photographic Industry	Fixer, Developer, Wash Water		450-3,000						P		P				
Steam Generation	Air Preheater Wash						.4-40	380-6,000							
	Boiler Fireside Wash						0-5	0-300							
	Acid Cleaning						400-1,000	4,000-10,000							
	Cooling Tower Blowdown					0-1,300									0-30

P = present, concentrations not reported.

TABLE 2. TREATMENT METHODS FOR METAL CONTAINING WASTEWATERS

Treatment Method	Status of Development	Comment on Application/Applicability
1. Hydroxide Precipitation	Commercially available.	Applied as either a batch or continuous process for wastewater treatment. Widely applicable. Limitation posed by metal complexing, does not remove alkaline and alkaline earth metals and certain anions. Hexavalent chromium must be reduced before treatment.
2. Sulfide Precipitation	Presently installed at Boliden's copper smelter in Sweden to control smelter effluent. Start-up scheduled for mid-1978. Also in operation at Furukawa's Ashio smelter in Japan.	Process has the advantage of controlling heavy metals in acidic solutions. The sulfide sludge can be recycled to smelting furnaces.
3. Ion Exchange	Commercially available.	Process can be used to control cations and anions. Process is not suitable as an end-of-pipe treatment. Additional treatment of secondary waste stream is required. It is suitable for concentrating wastes of high volume and low pollutant concentration and as a polishing process.
4. Evaporation Ponds	Commercially available.	Application is limited to arid regions. End products are easily resolubilized. Large land requirements are necessary.
5. Reverse Osmosis	Commercially available.	Pretreatment of wastewater is necessary to avoid membrane damage. Membrane scaling is a problem if insoluble compounds are present. Suitable for concentrating dilute waste streams. A concentrated reject stream is produced and requires further treatment. Process is not suitable as an end-of-pipe treatment.

(Continued)

TABLE 2 (continued).

Treatment Method	Status of Development	Comment on Application/Applicability
6. Activated Carbon	Commercially available.	Primarily suitable for removal of organics. Secondary removal of inorganics has been observed. It is unlikely that this process would be applied for treatment of inorganics alone. Disposal of exhausted carbon can result in the gradual release of the adsorbed compounds.
7. Ferrite Coprecipitation	Limited commercial use in Japan treating scrubber blowdown from a municipal incinerator. Also used by Nippon Electric Co.	Very good removal efficiency is achieved. This process appears to be an applicable treatment technology. However, it has only been applied on a commercial scale in Japan. The solid waste generated may be either recycled to smelting furnaces or landfilled.
8. Starch Complexing	Applied in pilot studies as polishing process.	Good removal efficiency is obtained. Metal compounds are released when starch decomposes. Starch manufacture requires carbon disulfide which is dangerous. Process is still in developmental stage but warrants further study.
9. Sodium Borohydride Reduction	Limited commercial use.	Process application is limited to reducing semi-noble and noble metals to the elemental state. Instability of sodium borohydrate in acidic solutions necessitates operation at pH 8.5 to 9.0. Process may be useful for small waste streams containing either valuable or difficult to remove metals, e.g., mercury. Not likely to be widely used because of high cost relative to hydroxide precipitation.

TABLE 3. PERFORMANCE OF TREATMENT TECHNOLOGIES

Treatment Method	Cost	Control Effectiveness			Energy Requirement	Residues Produced
		Element	Inlet mg/ℓ	Outlet mg/ℓ		
1. Hydroxide Precipitation	Capital Cost:* $0.343/liter/day ($1.3/gallon/day) Operating and Maintenance Cost: $700./day for 3.785 x 10^6 liters/day (1 million gallons/day) capacity and 1 gram per liter lime dosage rate See Figures 4 and 5.	Arsenic	.2-.5	.83	Energy users are: lime feeders, wastewater pumps, clarifier agitator drive, sludge rake drive, and vacuum filter. Energy consumption is 8 kWh per 3,785 liters (1,000 gallons) treated and 1 mg/ℓ lime dosage. 14 kWh per 3,785 liters (1,000 gallons) treated and 1,500 mg/ℓ lime dosage.	Solid metal hydroxides. Compounds will redissolve in acidic environment.
		Cadmium		.0007		
		Chromium(III)	1300	.06		
		Copper	204-385	.2-2.3		
		Lead	.5-25	.01-.03		
		Manganese		.5		
		Nickel	5	.15		
		Zinc	16.1	.02-.23		
2. Sulfide Precipitation	Not given in literature. Should be similar to hydroxide precipitation.	Arsenic	.8-132	.05-24.4	Unknown. Energy requirement should be similar to those given for hydroxide precipitation.	Metal sulfides are produced as end products. Most sulfides are insoluble in acidic solutions. They can be recycled to sulfide processing smelters. Solubilization is possible upon oxidation to sulfates.
		Cadmium	.4-1.0	.008		
		Copper	50-115	.5		
		Mercury	.3-50	.01-.12		
		Nickel	.13-.29	.09-.51		
		Zinc	42	1.16		
3. Ion Exchange	Depends on capacity and solids concentration. See Table 12 for details. Installed capital costs: $0.063 to $0.719/liter/day ($0.24 to $2.72/gallon/day). Operating costs: $0.00018 to $0.00067/liter ($0.00067 to $0.00253/gal).	Cadmium	.1	.001	Pumps are only energy consumers. 1.1 kWh for 3,785 liters (1,000 gallons) treated.	Regenerant waste stream will contain high metals concentration. Low volume of the waste stream may make further treatment more economical.
		Chromium(VI)	8-10.7	0-.9		
		Copper	1.02	.03		
		Lead	.055-144.8	.0015-.53		
		Manganese	50	.046		
		Mercury	1.4-2.8	.005		
		Nickel	150-900	.01		
		Zinc	6	.4		
4. Evaporation Ponds	Depends on location and land cost. Capital cost: $1.49/liter/day ($5.6/gallon/day) assuming 76.2 cm (30 inches) evaporation a year and $1,000 per 4046 m^2 (acre).	Complete control if liner is used. Seepage of salts into groundwater is possible if liner breaks.			Only energy consumers are pumps. 0.5 kWh per 3,785 liters (1,000 gallons) of wastewater is reported.	Process produces salts which redissolve upon contact with water.

(Continued)

* 1 gallon = 3.785 liters

TABLE 3 (continued).

Treatment Method	Cost	Control Effectiveness			Energy Requirement	Residues Produced
5. Reverse Osmosis	Depends on feed characteristics, pretreatment, and desired conversion. Installed capital costs: $0.193 to $0.528/liter/day ($0.73 to $2.00/gal/day) capacity. Operating costs: $0.00017 to $0.00058/liter ($0.00066 to $0.00218/gal).		Inlet Conc. mg/ℓ	Product mg/ℓ	Pumps are major consumers. 8-10 kWh per 3,785 liters (1,000 gallons) of water for a 3,785,000 liter per day (100,000 GPD†) unit.	Process produces a concentrated aqueous effluent stream containing practically all incoming contaminants.
		Calcium	260	.4		
		Magnesium	170	.3		
		Iron	77	.4		
		Aluminum	12	.2		
		Sulfate	1340	.9		
		Manganese	43	.5		
6. Activated Carbon	Data needed.	Data needed.			Data needed.	
7. Ferrite Coprecipitation	Not available. Should be similar to hydroxide precipitation.		Influent mg/ℓ	Effluent mg/ℓ	Not available. Should be similar to hydroxide precipitation.	Solid ferrite with heavy metals coprecipitated.
		Mercury	7.4	.001		
		Cadmium	240	.008		
		Copper	10	.010		
		Zinc	18	.016		
		Chromium	10	.010		
		Nickel	1,000	.2		
		Manganese	12	.007		
		Iron	600	.060		
		Bismuth	240	.100		
		Lead	475	.010		
		pH				
8. Starch Complexing	Not available.	Copper	31.8	.007	Not available. Should be higher than those for hydroxide precipitation due to the high volume of the precipitate.	Concentrated acidic wastewater stream, if starch is regenerated. Exhausted starch, which decomposes if not properly stored.
		Nickel	29.4	.019		
		Cadmium	56.2	.009		
		Lead	104	.025		
		Chromium(III)	26	.003		
		Silver	54	.245		
		Zinc	33	.046		
		Iron	27.9	Not detectable		
		Manganese	27.5	1.630		
		Mercury	100	.003		
9. Sodium Borohydride	Capital Cost: $0.18/liter/day ($0.67/gallon/day). Operating Cost: $0.002 to $0.007 liter ($0.007 to $0.026/gallon). Basis: 57,000 liters/day (15,000 gallons/day) plant. (PA-322)	Removes 0.45 to 1.81 kg TDS**/day (1.0 to 4.0 lbs/day). Reported effluent concentration is:			Not available.	Elemental metals.
		Mercury		.010		

† GPD - gallons per day.
** 1 gallon = 3.785 liters.

Hydroxide Precipitation

Hydroxide precipitation is widely used to treat acidic wastewater containing metals. It is sometimes applied as a batch process for wastewater quantities up to 1.89×10^5 ℓ/day (50,000 gal/day). Continuous operation may be used at any discharge rate.

Discharge concentrations for As, Cd, Cr, Cu, Pb, Mn, Ni, and Zn are cited in this literature (see Table 3). The effluent concentrations reported are below one ppm. Limitations in the removal efficiency are experienced if complexing agents are present in the wastewater which cause the metal ions to remain soluble at high pH values. Chromates (Cr^{+6}) also remain in solution at high pH values and must be reduced to Cr^{+3} in order for the hydroxide to form and precipitate.

Energy consumption depends on the lime dosage rate and therefore the metal concentrations in the wastewater. Lime addition rates of 100 and 1,500 mg/ℓ require 8 and 14 kWh of power respectively.

The cost of the process depends on the size of the treatment facility. Capital costs are $1.3 million for a facility treating 3.8×10^6 ℓ/day (1.0×10^6 gal/day). Operation costs are a strong function of the lime dosage rate required.

Metal hydroxides precipitated by this process are normally disposed of as a solid waste. However, they will redissolve if brought in contact with acidic water and therefore present a secondary waste problem.

Sulfide Precipitation

Sodium sulfide (Na_2S) is being used at Boliden Metall's primary copper smelter in Sweden to remove metals from a 200 m^3/hr (1.3 Mgal/day) wastewater stream. Arsenic, cadmium, lead, zinc, copper, cobalt, antimony, and selenium are present in the wastewater. As yet, however, no removal efficiencies or effluent concentrations have been reported.

Sodium hydrosulfide (NaHS) is being used at Furukawa Co., Ltd.'s Ashio copper smelter in Japan to treat sulfuric acid plant blowdown. Removal efficiencies of greater than 99 percent have been reported for arsenic, copper, cadmium, lead with effluent concentrations of 0.03, 0.03, 0.3, and 0.5 ppm respectively.

Energy requirements and economic data have not been published for the different sulfide processes. Both energy requirements and capital and operating costs should be similar to those for lime precipitation. Two factors make this process economically feasible. First, the ability to operate at low pH values (pH 4 to 5) lowers the neutralization cost. Second, the ability to recycle the precipitate to the smelting furnaces allows the metal and sulfur values to be recovered and eliminates the cost of solid waste disposal.

The sulfide sludge generated by this process can present a costly disposal problem if it cannot be sold or recycled to a smelter. Oxidation of the sludge would produce soluble sulfates which will dissolve in water.

Ion Exchange

Ion exchange equipment is commercially available. It is especially suited to polish streams of high volume and low pollutant concentrations. The costs of the process depend on capacity and solids concentration. For a 3.8×10^5 ℓ/day (100,000 gal/day) plant treating water containing 500 ppm solids, the installed capital cost is $174,000. The yearly operating costs are $73,000. Effluent concentrations below one ppm could be expected. The estimated power requirement is 1.1 kWh per 3,785 liters (1,000 gallons treated.

The ion exchange operation creates a low volume, high concentration aqueous effluent stream which needs additional treatment.

Evaporation Ponds

The application of evaporation ponds is limited to arid regions. Costs depend on land availability and evaporation rate. A cost figure of $1.2 million to treat a stream of 570 ℓ/min (150 gpm) is cited, assuming an evaporation rate of 76.2 cm/year (30 inches/year) and $1,000 per acre. The only power consumption is for the pumping requirements which amount to 0.5 kWh/3,785 liters (0.5 kWh/1,000 gal). The process produces salts which will redissolve upon contact with water.

Reverse Osmosis

Reverse osmosis (RO) is a commercially available process which produces a clean product stream suitable for reuse or discharge and a contaminated reject stream requiring further treatment before discharge. Therefore, RO cannot be considered an end-of-pipe treatment.

The removal efficiency and costs associated with RO systems depend on feed characteristics, pretreatment, and desired conversion. Data show that Al, Cu, Fe, and Mn are rejected at rates greater than 90 percent. Installed capital costs for RO systems range from $0.19 to $0.53 per liter per day ($0.73 to $2.00 per gallon per day) of treatment capacity. Reported operating costs range from $0.17 to $0.58 per thousand liters ($0.66 to $2.18 per thousand gallons) treated. Of this operating cost, the energy requirement is minimal. For a 380,000 ℓ/day (100,000 gpd) RO unit, the estimated energy requirement is 8 to 10 kWh per 3,785 liters (1,000 gallons) of water treated.

Activated Carbon

Beds of activated carbon are normally used to adsorb organic compounds from water effluents. However, secondary removal of metals has been observed.

Energy is required for the absorption step for pumping to overcome the pressure loss through the carbon beds. The estimated power requirement for pumping is 0.32 kWh per 3,785 ℓ (1,000 gallons). This number is only approximate since the actual amount will vary with each system design and total dynamic head requirements. The electrical power required is estimated to be 5.8 kWh per 37.3 kg (100 pounds) of carbon regenerated. Cost data is not available for an application designed to remove metals from an acidic waste stream.

The exhausted carbon bed is the only secondary waste. Disposal in a landfill presents a potential problem because the adsorbed compounds can be gradually released.

Ferrite Coprecipitation

Ferrite coprecipitation is an effluent control approach which was developed and is industrially applied in Japan. The metals concentrations achieved in treated effluent water are in the 1 to 200 ppb range (see Table 3). The precipitated hydroxides are reportedly embedded in ferrites which are only slightly soluble. The ferrites are magnetic and can be removed either by filtration or magnetic separation.

Process cost and energy requirements are not available.

Starch Complexing

Starch complexing was applied in pilot studies as a polishing process. Good removal efficiencies were reported (see Table 3). However, disposal of the spent starch that is generated after absorbed compounds are released results in a concentrated stream which must be treated by other means. In addition, poisonous carbon disulfide is used in the starch generation process.

Cost data and power requirements for the process are not available.

Sodium Borohydride

Sodium borohydride exhibits a strong reduction potential. It is used commercially for electrolytic nickel plating. It is capable of reducing noble and semi-noble metals to the elemental state at a solution pH of 8.0 to 9.0. The reported effluent concentration achieved for mercury removal is 0.01 mg/ℓ.

Capital costs are reported as $667 per 3,785 liters (1,000 gal). Operating costs are between 1.8 and 7.1 cents per 1,000 liters (6.7 to 26.7) cents per 1,000 gal). Power requirements are not reported.

Elemental metals are the solid residues generated by this process. They can be either sold or recycled to recover the metal values. The boron remains soluble as a borate and exits with the discharge stream. Boron effluent concentrations have not been reported.

SOURCES OF ACIDIC WASTEWATER IN THE NONFERROUS METALS INDUSTRY

The sources of wastewater in the primary and secondary copper, lead, and zinc industries are listed in Table 4. In the primary industry, wastewater emanates from:

- mining,
- concentrating,
- smelting,
- refining, and
- air pollution control.

The elements and concentrations shown in Table 4 are similar to wastewater discharged by other industrial sources (see Appendix).

Data for the secondary industries are rather scarce. Metal concentrations were found only for the grinding and gravity separation process and the ingot cooling and quenching operations. No data were found for secondary lead and zinc industry effluents.

TABLE 4. WASTEWATER SOURCES IN THE NONFERROUS METALS INDUSTRY

Industry	Process/Unit Operation	Nature of Discharge (mg/ℓ)													
		Al	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Se	Sn	Zn
Primary Copper	Mining (400-3800 m^3/day)			<.01	<.02		.9-1	<.1	<.0001	1-2	<.5	<.05	.1		.1-3
	Ore flotation 100-500 m^3/ton of concentrate		~.1	.07	.02-.05		high	.1-2		.05-5	.01-3	.05-3	.003-.02		.05-850
	Slag Flotation			.05-6	.001-.04		.05-.1	.03-340			.04-7	.001-.2	.005-.5		.02-36
	Sulfuric Acid Blowdown .1-10 x 10^6 ℓ/day			.004-.1	.0002-.03		.0001-188	.001-.11			.005-.3	0-.003	0-.03		.002-.4
	DMA Unit - Prescrubber	Similar to Sulfuric Acid Blowdown													
	Arsenic Plant Washdown Water			310	1		88	9			8	.75	.04		37
	Anode Cooling Water (Concentration change)	.1		.01			8.5								.25
	Electrolytic Refining Spent H_2SO_4 Electrolyte			500-12,000			50,000					2,000-20,000			
Primary Lead	Mine Drainage				<.002-.06	<.01-.2	.004-700	<.02-2.5		<.02-57	.02-.07				.008-.04
	Concentrating				.005-.01	.002-.02	.01-.4	.03-.5	<.001	.03-.2	.1-2				.1-.5
	Contact Acid Plant	Similar to effluent in primary copper industry													
	Slag Fuming										.2	.02			.4
Primary Zinc	Mining	No data.													
	Concentrating				.005-.01	<.02-.7	<.02-.4	.05-.5	.0001-.1	<.02-.08	<.1-1.9				.1-.5
	Horizontal Retorting	No data.													
	Vertical Retorting	No data.													
	Electric Retorting	No data.													
	Other Sources	No data.													
Secondary Copper	Grinding & Gravity Separation			<.02-.001	.07-1.7	.12	.07-1250	.007-164	.0003-.002	.05-43	.2-917	.03-18			.2-983
	Insulation Burning Unit	No data.													
	Steam Distillation Unit	No data.													
	Hydrothermal Hydrogen Reduction	No data.													
	Ingot Cooling & Quenching			<.02	<.05	.02-.07	.6-3.4	.6-1.6		.133	.5-4.3	.1			.3-18
	Electric Crucible Smelting Metal Cooling Water	No data.													
	Fire Refining Metal Cooling Water	No data.													
	Electrolytic Refining Spent Electrolyte Slimes	No data.													
Secondary Lead	Battery Breaking	No data.													
	Leaching	No data.													
	Other Operations	No data.													
Secondary Zinc	Sodium Carbonate Leaching	No data.													
	Other Operations	No data.													

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

From the results presented in Section 3 and in the report Appendix, it is clear that the metal concentrations found in nonferrous metal industry wastewaters are similar to those found in other industries. From this, it might be concluded that the common treatment technologies, hydroxide precipitation and evaporation, might be applicable to the nonferrous metals industry effluents. However, the results also show that the waste streams in the metals industry are poorly characterized.

Source characterization, therefore, is recommended before a final judgement can be made concerning the most applicable wastewater treatment technology. This is especially true in the case of new treatment technologies where the precipitation kinetics, solution equilibria, and particle settling properties may not be well understood for solutions containing many metal ions.

Based on the data presented in Table 5, it appears that with the hydroxide precipitation, sulfide precipitation, and ferrite coprecipitation processes the existing EPA drinking water and irrigation standards can be met. The results presented also indicate that two processes, sulfide precipitation and ferrite coprecipitation, seem particularly applicable to the nonferrous metals effluents. Recycling the solid wastes generated by these processes to the smelting furnaces results in enhanced metals recovery while eliminating the solid waste disposal problem. However, the real effectiveness, energy requirements, and economic data related to both the sulfide and ferrite processes are not well documented. Field test programs to develop these data are necessary before a final judgement concerning the applicability of these two recommended processes can be made.

The results are not conclusive with respect to either the starch complexing or sodium borohydride processes. Starch complexing has not been applied on a commercial scale. Commercial use of sodium borohydride has been limited. This process may be of interest in other small scale applications where precious or hard to remove metals must be recovered in elemental form. At this time, these processes are not applicable to the major wastewater treatment problems in the nonferrous metals industry. However, additional testing of these processes is recommended, especially in applications specific to the smelting industry.

Field test programs could be completed in two ways. For the sulfide, ferrite, or borohydride processes, where commercial-scale plants are already built, a test could be developed to measure the removal effectiveness of the

TABLE 5. COMPARISON OF TREATMENT PROCESS DISCHARGE CONCENTRATIONS WITH WATER QUALITY STANDARDS (mg/ℓ)

	As	Ba	B	Cd	Cl	Cr	Cu	F	Fe	Pb	Mn	Mo	Se^-	Ag	Zn	NO_3^-	$SO_4^=$	TDS
EPA Primary* & Secondary** Drinking Water Standards	.05	1	-	.01	250	.05	1	-	.3	.05	.05	-	.01	.05	5	10	250	1000
Irrigation Standards (NA-199)	2	-	.75	.01	-	.1	.2	2	5	5	.2	.01	.02	-	-			5000
Hydroxide Precipitation	.03			.0007		.06	.2			.01	.5				.02			
Sulfide Precipitation	.05			.008			.5								1.2			
Ion Exchange				.001			.03			.002	.05				.4			
Reverse Osmosis								.4			.1						.9	
Activated Carbon								No data available.										
Ferrite Coprecipitation				.008		.01	.01		.06	.01	.007				.02			
Starch Complexing				.009		.003	.007		0	.03	1.6			.2	.05			
Sodium Borohydride			†					No data available.										

* Federal Register, December 24, 1975.

**Federal Register, March 31, 1977.

† May exceed standard for boron discharge.

specific plant design. For more general studies of either the sulfide, ferrite, starch complexing, or sodium borohydride processes, small skid-mounted units would be ideal for testing at different sites. These small units could examine different dosage rates, pH operating ranges, residence times, and could alter the feed conditions without interfering with plant operations. In addition, by treating a small slip stream the cost of both the test equipment, instrumentation, and raw materials would be minimized.

This type of equipment would also be useful for examining synthesized waste streams, especially in conjunction with laboratory investigations. After studying the chemical equilibria and precipitation kinetics of a particular treatment process in the laboratory, the skid-mounted unit could be used to simulate actual field conditions. These types of tests would provide data on the effectiveness of each wastewater treatment process before commercial-sized plants are built.

The results of this study also indicate that ion exchange, reverse osmosis, and activated carbon are not applicable as end-of-pipe treatment processes for the nonferrous metals industry unless the small concentrated waste stream could be either recycled to the smelter or treated. Extensive pretreatment of smelter wastewaters would be required with these processes which would reduce any cost effectiveness gained by concentrating the wastewater streams using either process. It is doubtful that activated carbon would be used in any applications where metals removal was the major problem.

SECTION 5

INDUSTRIAL SOURCES OF ACIDIC WASTEWATER CONTAINING METAL

The important results of the investigation into the sources of industrial wastewater were that:

- no previously unknown wastewater treatment technology was being used by the industries studied, and
- the available literature data on the quantity, metal contaminant concentration, and treatment technology effectiveness were very sparse.

Matrix Table 6 is a brief summary of the data avilable from work performed by IERL and other investigators showing the metals found in various industrial wastewater. It should be noted that some of the metals listed in this table are present in trace quantities (<100 ppm) and are not specifically treated for removal.

The report Appendix contains a more specific list of the sources of acidic wastewater and the reported concentration for each metal. Table 6 quantifies the metal contamination in each industry based on data found by a literature search. It is not a comprehensive list of wastewater sources. Rather, it lists some of the significant sources, the published metal concentrations in the untreated wastewaters, and the literature references. It was the intent of this investigation to identify and characterize some of the common industrial sources of acidic wastewater from the standpoint of quantity, metal concentrations, and treatability. It was then hoped that by comparing these sources with those in the nonferrous metals industry it would be possible to determine which wastewater treatment technologies could be transferred between industries.

However, it was clear from the small amount of information available that acidic wastewater characteristics are variable and differ from source to source. For example, it is not reasonable to expect that spills from the manufacture of fertilizers could be treated in the same fashion as acid mine drainage though similarities do exist. Cooling tower blowdown is a good example of a wastewater stream common to many industries.

TABLE 6. INDUSTRIES AND ASSOCIATED HEAVY METALS

INDUSTRY	Al	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Se	Sn	Zn
Cement	X				X		X			X				
Electronics				X	X	X		X		X	X			X
Explosives									X	X				
Glass and Ceramics			X	X	X									X
Inorganic Chemicals	X		X	X	X		X	X		X			X	X
Leather Tanning/Finishing			X		X									
Metal Finishing	X	X		X		X		X			X			X
Mining	X		X	X		X	X	X	X	X	X			X
Organic Chemicals	X		X	X		X	X	X		X			X	X
Paint Formulating, Ink Formulating			X	X	X	X	X		X	X				X
Petroleum Refining	X		X	X	X	X	X	X		X	X			X
Photographic		X						X		X				
Plywood, Hardboard, Wood Preserving			X		X	X								X
Pulp and Paper Mills					X	X		X		X	X		X	X
Steam Generation					X	X	X			X				
Steel and Iron (including ferro-alloy)	X				X	X	X	X	X	X	X		X	X
Textile					X	X								X
Tires					X									X
	Al	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Se	Sn	Zn

X - identified in process wastewater streams from this industry.

The most common wastewater treatment technologies used by the industries listed in Table 6 are hydroxide precipitation and evaporation. Specific applications use ion exchange, activated carbon, and reverse osmosis to purify some water streams for use as either process or boiler feed water. The sodium borohydride reduction process has been used to remove precious and hard to remove metals from small industrial wastewater streams. The sulfide precipitation and ferrite coprecipitation processes have been used in limited applications in Europe and Japan but little data is available on the effectiveness, costs, and energy requirements for these commercial-scale applications. These and several other processes are described in more detail in the following section.

SECTION 6

TREATMENT METHODS FOR WASTEWATER CONTAINING METALS

INTRODUCTION

In this section treatment technologies for removing metals from wastewaters are evaluated. The treatments which are assessed include:

- hydroxide precipitation,
- sulfide precipitation,
- ion exchange,
- reverse osmosis, and
- evaporation ponds.

These technologies were chosen based on their ability to adequately remove metals present in industrial wastewaters. The assessment of treatment techniques includes:

- a brief process description including the basic treatment steps and the chemistry or mechanism by which metals are removed,

- control effectiveness which documents reported removal levels for certain metals,

- energy requirements which give estimates of the energy consumed during operation of a treatment system,

- economics which present estimates of the capital and operating costs, and

- secondary process emissions which qualitatively describe the air, liquid, or solid emissions which are generated during the operation of each treatment system.

Following this assessment, a description of other treatment technologies for metals control in industrial effluents is given. The technologies discussed include:

- activated carbon,
- ferrite coprecipitation,
- starch complexing, and
- sodium borohydride reduction.

The evaluation of these treatment technologies is limited to a brief description of the processing scheme, removal mechanism or chemistry, metals removal effectiveness, and potential secondary pollutants. These processes, generally, are not as well developed in the field of wastewater treatment for metals removal. Consequently, sufficient information was not available to evaluate their applicability to metals removal from industrial effluents.

HYDROXIDE PRECIPITATION

Hydroxide precipitation for heavy metals removal from streams is both an effective and economical treatment technology. The treatment converts soluble metals into hydroxide compounds. The metals can then be separated from the liquid through sedimentation and/or filtration. The most commonly used precipitating agents are lime [CaO or $Ca(OH)_2$] and caustic ($NaOH$).

Hydroxide precipitation has been applied in treating industrial wastewaters. The following is a list of some of the industries which use this technology:

- nonferrous metal processing,
- ore mining and dressing,
- utility power generation,
- metals plating, and
- battery manufacturing.

Process Description

Hydroxide precipitation removes metal contaminants from wastewater by forming metal hydroxide compounds and precipitating them from solution. To be successful, the precipitation step depends primarily upon two factors:

1) sufficient available hydroxide to drive the precipitation reaction to completion, and

2) removal of the resulting solids from the treated water.

To accomplish this, a continuous wastewater treatment process utilizing hydroxide precipitation consists of four basic steps:

1) pH adjustment - where the hydroxide feed is mixed with the wastewater and the pH is adjusted,

2) flocculation - where the reactions forming the metal hydroxides are given time to reach a point where sufficient metals removal is accomplished and floc growth occurs,

3) clarification - where the water is passed through a quiescent zone allowing the floc to settle, and

4) filtration and pH adjustment - where the overflow from clarification is filtered to remove remaining solids and pH is adjusted to meet discharge regulations.

An example of a flow diagram for a continuous flow hydroxide precipitation system is shown in Figure 1.

In the first step the hydroxide precipitating agent is thoroughly mixed with the wastewater stream. The sources of hydroxide used in industrial applications of this technology are quicklime (CaO), hydrated lime [$Ca(OH)_2$] or caustic soda (NaOH). The reactions which begin in the flash-mix tank and which result in formation of the insoluble metal hydroxides are given below:

for quicklime -

$$CaO + H_2O \rightleftarrows Ca(OH)_2 \tag{6-1}$$

$$M^{++} + Ca(OH)_2 \rightleftarrows M(OH)_2\downarrow + Ca^{++} \tag{6-2}$$

or hydrated lime -

$$M^{++} + Ca(OH)_2 \rightleftarrows M(OH)_2\downarrow + Ca^{++} \tag{6-3}$$

for caustic soda -

$$M^{++} + 2NaOH \rightleftarrows M(OH)_2\downarrow + 2Na^{+} \tag{6-4}$$

where M^{++} is the metal cation removed.

Dosages of the precipitating agent fed into the flash-mix tank are determined by the characteristics of the specific wastewater being treated. Those parameters affecting dosage rates include inlet water pH, temperature, hardness, metals concentration, and the desired system operating pH. The effect of pH on metal hydroxide solubilities is shown in Figure 2. Prediction of the proper dosages from an analysis of the wastewater is difficult and could lead to inefficient operation of the system. A method of determining dosages is to perform laboratory jar tests. These tests also can determine important design and operating information for the system such as:

- optimum operating pH,
- most effective alkali feed and coagulant aid,
- flash mix and flocculation time, and
- settling time.

The resulting data provide the necessary basis for determining the economics of the process for treating a given wastewater.

From the mixing step, the waters pass to the second step which is flocculation. Finely divided precipitates or microflocs which were formed in the mix tank are conditioned in the flocculation zone. Here gentle agitation and circulation are used to agglomerate the microfloc to clumps of

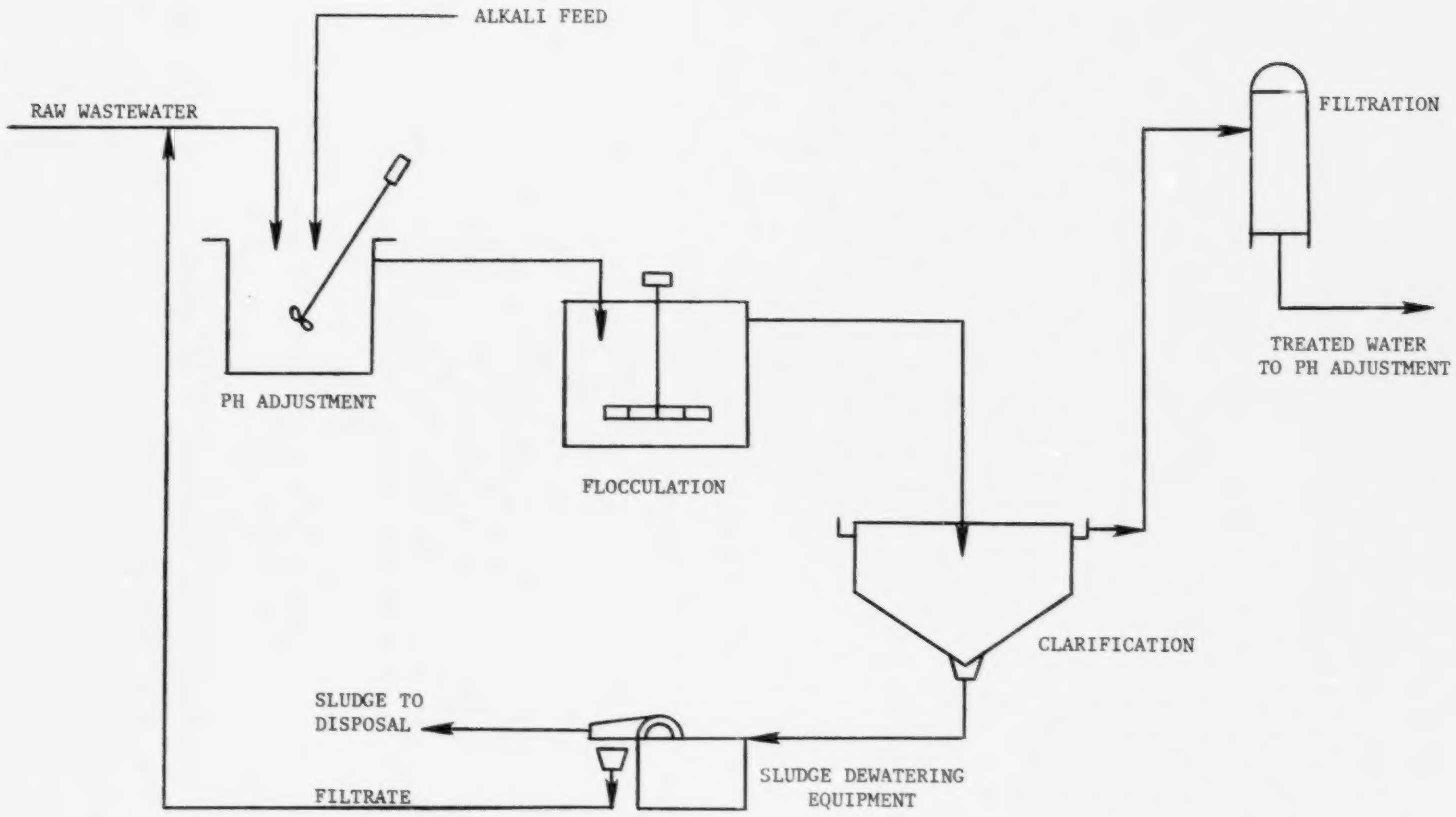
ALKALI FEED
RAW WASTEWATER
FILTRATION
PH ADJUSTMENT
FLOCCULATION
TREATED WATER
TO PH ADJUSTMENT
CLARIFICATION
SLUDGE TO
DISPOSAL
FILTRATE
SLUDGE DEWATERING
EQUIPMENT

Figure 1. Typical continuous flow hydroxide precipitation treatment system.

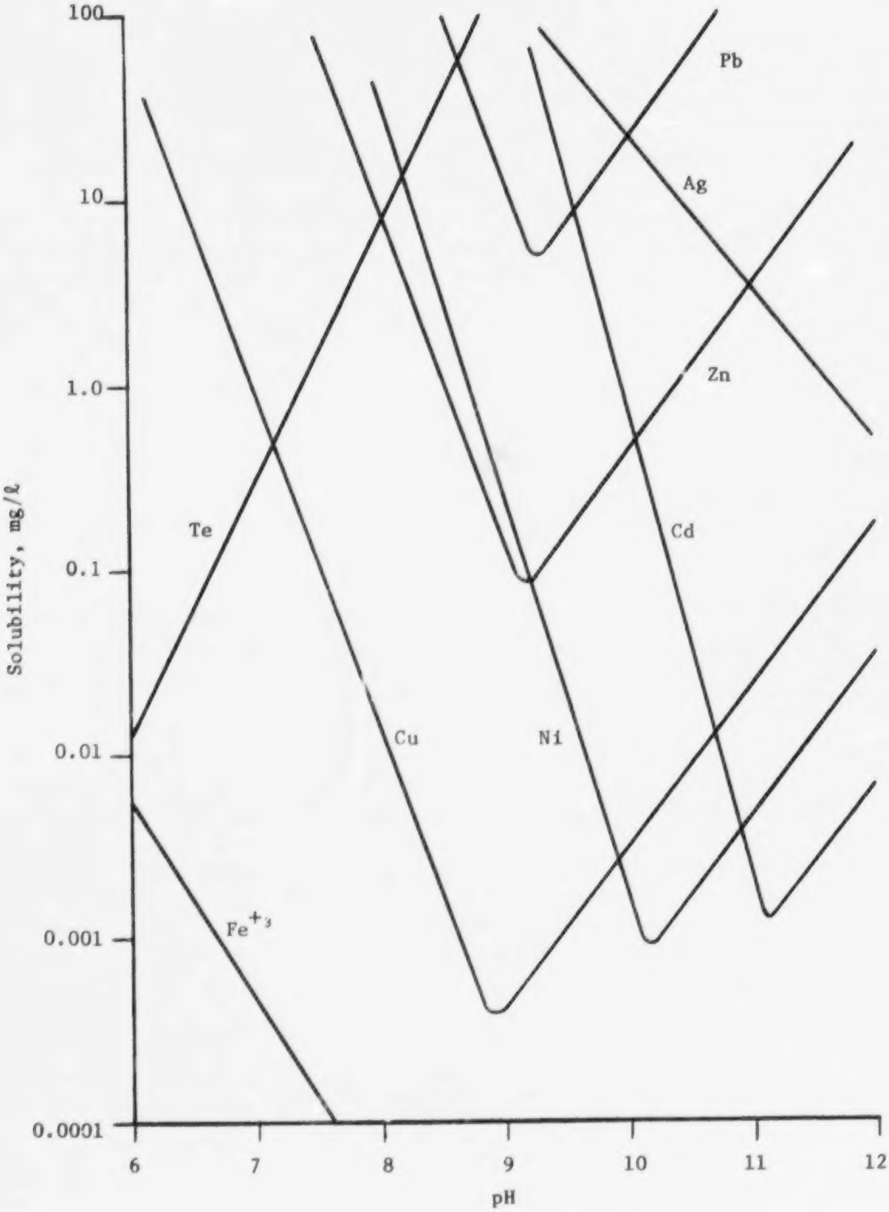

Figure 2. Theoretical solubilities of metal hydroxides as a function of pH.

settleable size. Coagulant aids added in the mix tank can hasten coagulation or growth of the microfloc. Time is also provided in the zone for the reaction between the precipitating agent and the dissolved metals to reach equilibrium.

After coagulation and flocculation the water is sent to clarification where it is passed through a quiescent zone where the floc is allowed time to settle out of the water. Settled floc accumulates on the bottom of the clarifier as a sludge. The sludge is usually mechanically raked into a sump from which it is drawn off as a slurry for dewatering and disposal.

The treated water which is collected as overflow from clarification is sent to filtration to further separate solids. These filters are generally designed for gravity flow and consist of a sand bed or multimedia granular bed. Following filtration the water may need to be treated for pH adjustment to satisfy discharge regulations which usually require a pH of 6 to 9.

An alternative processing scheme to the continuous flow treatment described above is batch treatment. Batch systems are generally preferred when wastewater flows are small, periodic, or when wastewater characteristics are highly variable. These systems can be economically designed for flows up to 50,000 gal/day but systems with capacities up to 100,000 gal/day are feasible (LA-A-347). A typical batch chemical precipitation facility is shown in Figure 3.

The design of a batch treatment process usually consists of two tanks, each with the capacity to treat the total wastewater volume expected during an operating period. This redundancy provides sufficient backup capability to insure consistent and adequate treatment.

During a process operating period, a tank is filled with the wastewater, agitated to a homogenous mixture, and a sample is taken to determine the quality. The wastewater parameters mentioned earlier determine the chemical dosage requirements. The tank contents, including the precipitating agent, are mixed and agitated for a sufficient period, usually approximately 30 minutes, to insure complete precipitation. After the reaction has reached equilibrium, the tank contents are allowed to settle for 2 to 4 hours and a second sample is taken to insure that sufficient treatment has been accomplished (LA-A-261).

Once the desired quality is attained, the clear liquid is decanted and discharged or treated further. Settled sludge is retained in the bottom of the reactor and serves as seed for the next batch. Excess sludge must be withdrawn periodically (LA-A-261).

Control Effectiveness

Hydroxide precipitation is capable of removing certain metals found in acid wastewaters. Among the metal ions removed are arsenic, cadmium, copper, trivalent chromium, iron, manganese, nickel, lead, and zinc. Table 7 presents reported residual concentrations to which hydroxide precipitation can

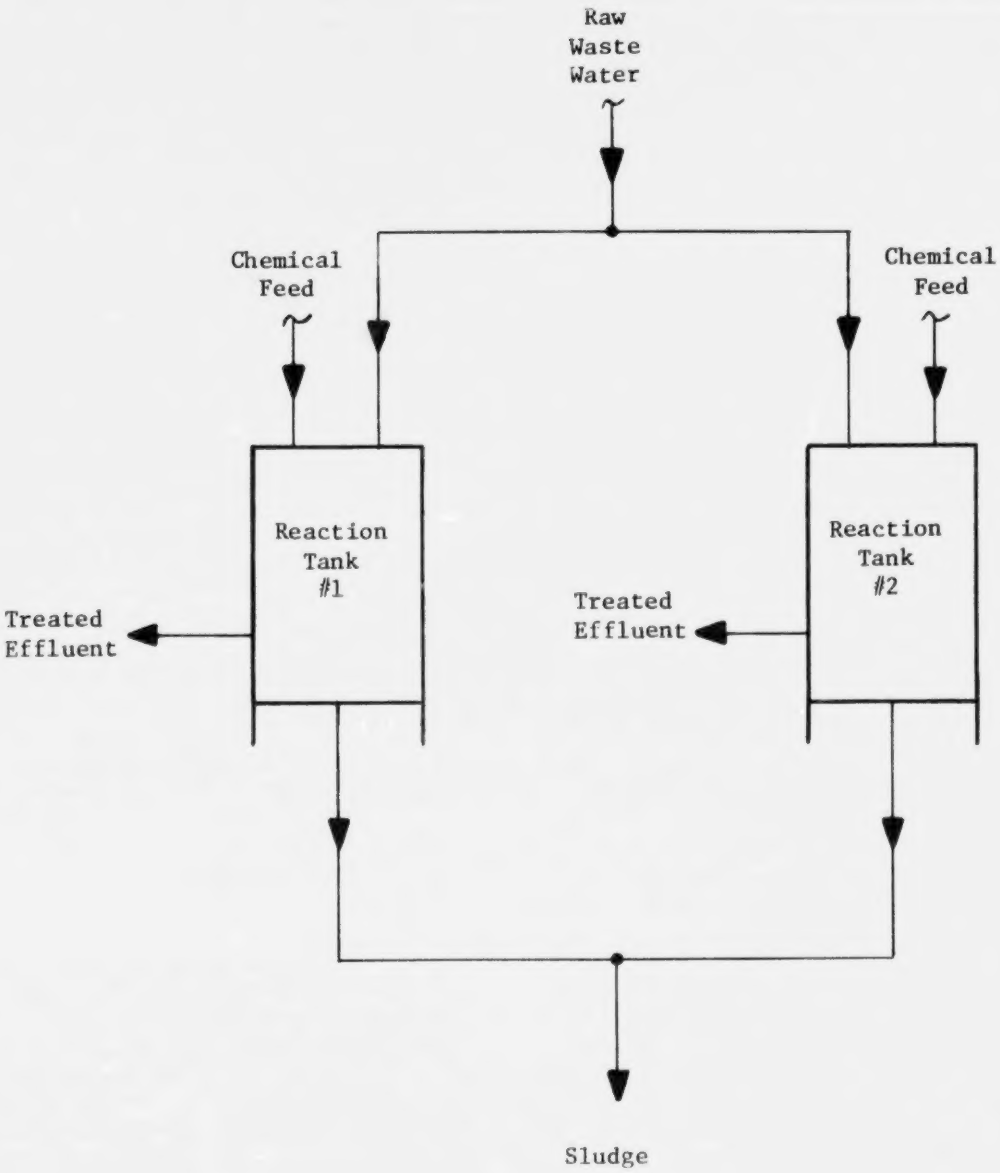
Raw Waste Water
Chemical Feed
Chemical Feed
Reaction Tank #1
Reaction Tank #2
Treated Effluent
Treated Effluent
Sludge

Figure 3. Typical batch process chemical precipitation treatment facility.

remove these metals. This information is based upon application of hydroxide precipitation to various industry wastewaters. It is important to note in Table 7 that in some cases, e.g., lead, cadmium, and zinc, the residual concentrations reported are lower than the theoretical solubilities of the pure element in water (see Figure 2). Several phenomena influence the effectiveness of precipitation, e.g., ionic strength, coprecipitation, and adsorption. These phenomena will ultimately determine the residual concentrations in specific applications, especially in solutions containing several metal ions.

TABLE 7. HYDROXIDE PRECIPITATION METAL REMOVAL EFFECTIVENESS

Metal	Inlet Concentration (mg/ℓ)	Residual Concentration (mg/ℓ)
Arsenic	0.2 - 0.5	0.03
Cadmium	ND	0.0007
Chromium, trivalent	1300	0.06
Copper	204 - 385	0.2 - 2.3
Iron	10	0.1
Lead	0.5 - 25	0.1 - 0.03
Manganese	ND	0.5
Nickel	5	0.15
Zinc	16.1	0.02 - 0.23

Source: PA-322

Energy Requirements

Energy usage for a hydroxide precipitation facility which treats acid wastewaters will vary according to site specific design parameters. Estimates for the energy required to operate an example precipitation system are presented here, though, to indicate the relative magnitude of its energy usage compared to other wastewater treatment technologies. The estimates are for a 500,000 gal/day system using lime as the hydroxide precipitating agent. Primary energy users are the lime feeders, wastewater pumps, clarifier agitator drive, sludge rake drive, and vacuum filter. For a 100 mg/ℓ lime dosage the system consumes about 8 kWh of electricity per 1,000 gallons of wastewater treated. For a dosage of 1,500 mg/ℓ, the energy requirements increase to 14 kWh per 1,000 gallons (CO-R-685).

Economics

The costs associated with wastewater treatment by lime precipitation are discussed below. Figures 4 and 5 present curves for lime precipitation capital costs and operation and maintenance costs (1977 dollars). The equipment on which the cost curves are based include a lime feeder, flash mix tank,

Equipment List:
- Lime Feeder
- Flash Mix Tank
- Clarifier/Flocculator
- Sludge Thickener
- Vacuum Belt Filter
- Multi-media Filter

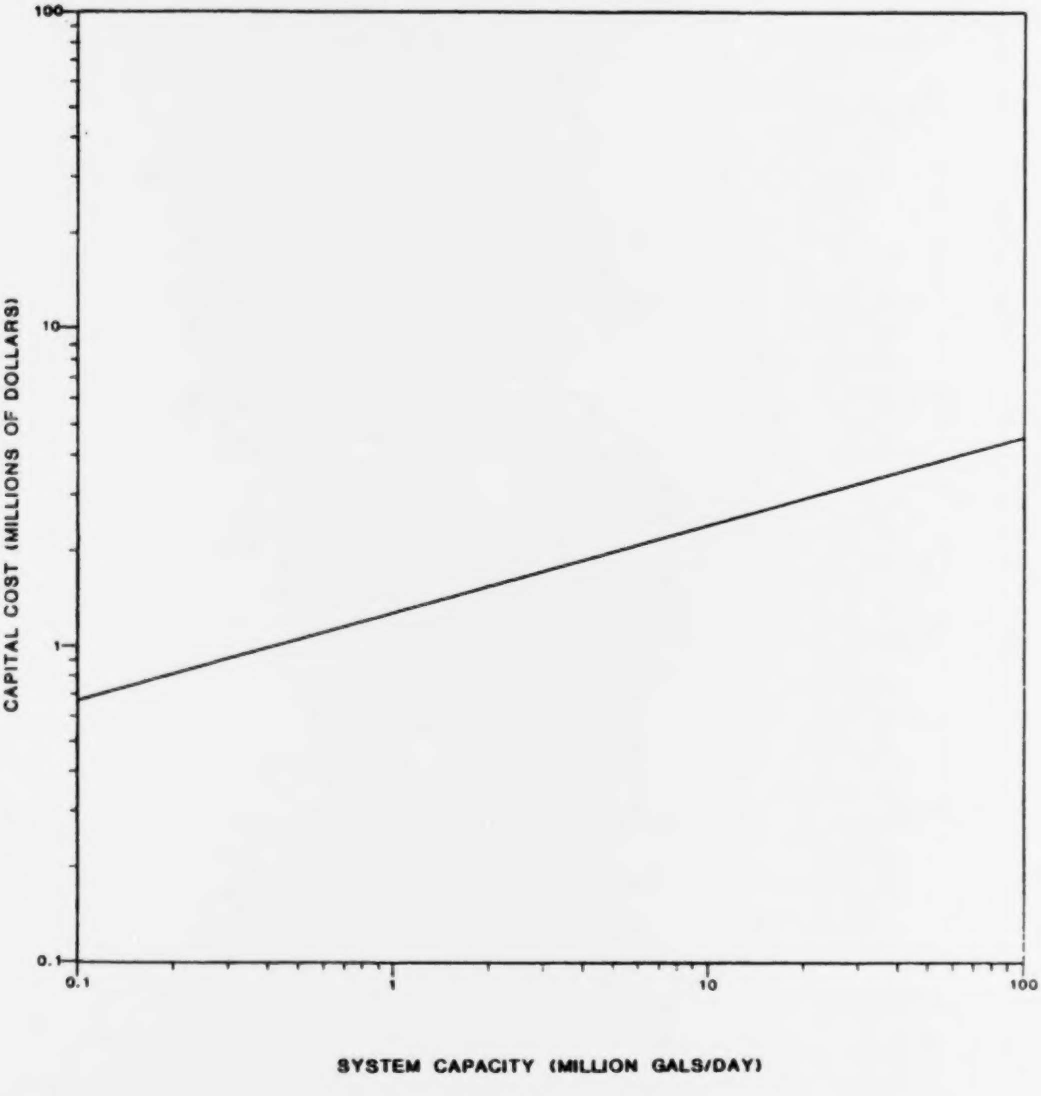

Figure 4. Lime precipitation installed capital costs.

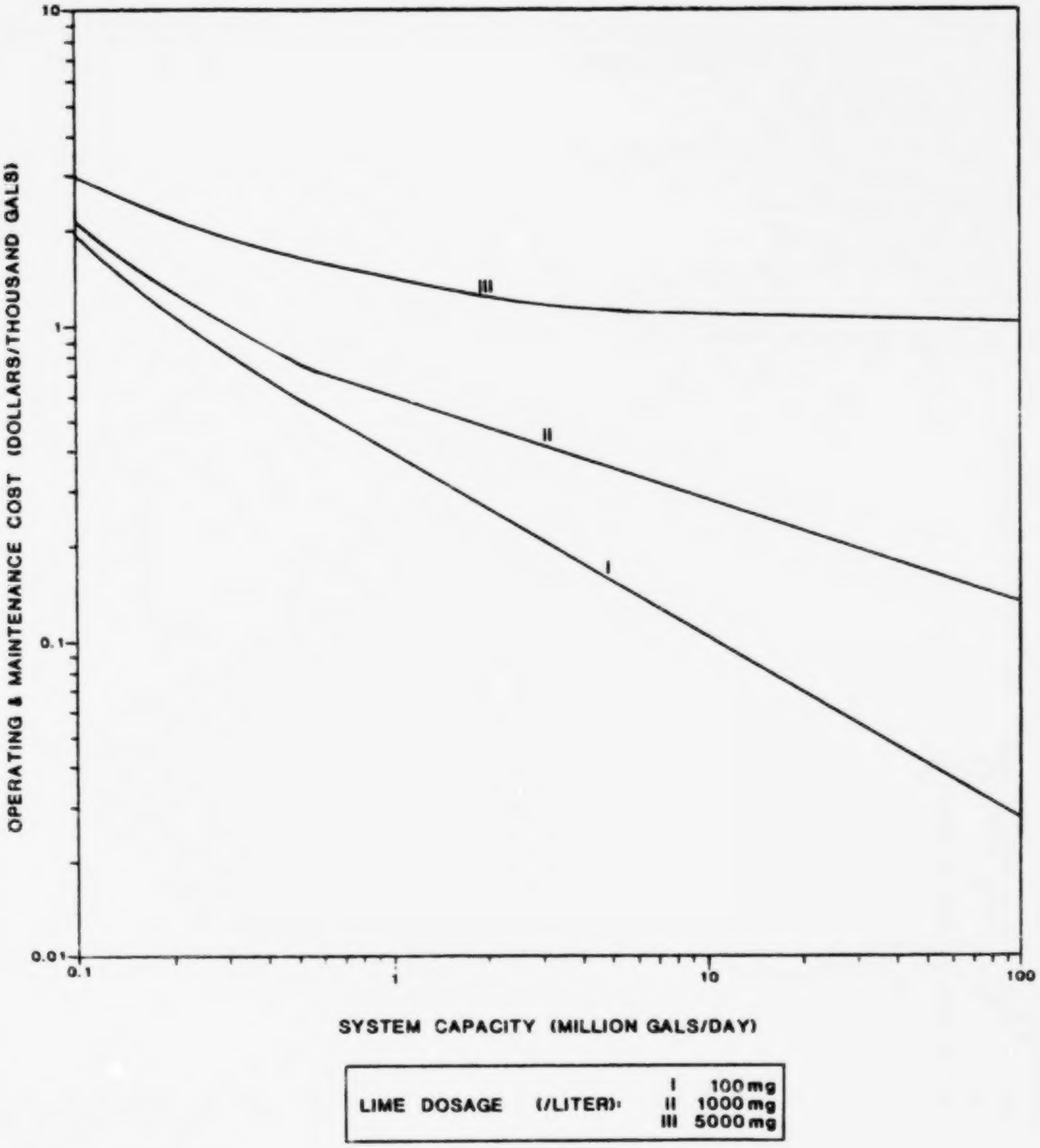

Figure 5. Lime precipitation operating and maintenance costs.

clarifier/flocculator with sludge recycle, sludge thickener, vacuum belt filter for sludge dewatering, and a filter for final effluent polishing. This equipment selection represents the most capital intensive treatment system. If effluent standards could be met and if land were available, settling ponds and lagoons could be utilized. Capital costs and operating and maintenance costs might be substantially decreased with such an arrangement since it involves less equipment. However, for the application of precipitation for metals removal, the low concentrations may require the more expensive arrangement to obtain adequate overall removals. The costs presented in Figures 4 and 5 do not include the costs of disposing of the dewatered sludge.

The effect of different lime requirements on the operating and maintenance costs due to varying inlet stream hardness, operating pH, and metals concentration is shown in Figure 5. Curve I represents a lime dosage of 100 mg/ℓ. Curve II is for a dosage of 1,000 mg/ℓ and Curve III for a dosage of 5,000 mg/ℓ (CO-R-685).

Secondary Process Emissions

The precipitated solids formed in the clarifier represent a secondary waste when separated from the wastewater. The sludge is usually processed by dewatering in a thickener and vacuum filter or filter press to reduce its volume prior to disposal. However, if land is available, it may be sent directly from the thickener to ponds for disposal. Care must be exercised to prevent the metals from being leached or discharged from disposal sites or ponds. Lagoon or pit bottoms can be lined with natural clays or artificial liners to prevent excessive amounts of leachate from reaching the groundwater. Underdrains may also be considered for collection and transportation of leachate from disposal sites. Also, chemical additives can be used to help control the mechanism by which metal sludges are leached from a landfill.

SULFIDE PRECIPITATION

Sulfide precipitation of the metallic ions present in acidic wastewaters is a viable treatment technology. Inherent environmental problems associated with it have resulted in very few industrial installations, however. As with hydroxide precipitation, sulfide precipitation relies upon converting soluble metals into a slightly soluble compound, in this case metal sulfides. The precipitated compounds can then be separated from the liquid through sedimentation and filtration. The sulfide reagents commonly used are: sodium sulfide (Na_2S), sodium hydrosulfide (NaHS), calcium sulfide (CaS), and barium sulfide (BaS).

Industrial applications of sulfide precipitation have been limited, as mentioned, due to environmental problems. The following is a list of those industries to which this technology has been applied for wastewater treatment:

- Ore mining and dressing,
- Nonferrous metal processing,
- Chlor-alkali production, and
- Phosphoric acid production.

Process Description

The treatment of acidic wastewaters for metals removal by sulfide precipitation is similar to hydroxide precipitation in that a slightly soluble metal compound is formed which can be easily separated from solution. To be successful, sulfide precipitation depends primarily upon two factors:

1) sufficient available sulfide to drive the precipitation reaction to completion, and

2) removal of the resulting solids from the treated water.

To accomplish this, a continuous flow sulfide precipitation facility consists of four basic steps:

1) pH adjustment and flash mixing - where the stream pH is raised by alkali addition and the sulfide precipitating agent is mixed with the wastewater,

2) flocculation - where the reactions forming the metal sulfides are given time to reach a point where sufficient metals removal is accomplished and floc growth occurs,

3) clarification - where the treated wastewaters are passed through a quiescent zone allowing the precipitate or floc to settle out, and

4) final effluent filtration and pH adjustment - where the treated overflow from clarification is filtered to remove any unsettled solids and the stream pH is adjusted to meet discharge regulations.

An example of a flow diagram for a continuous flow sulfide precipitation system is shown in Figure 6.

In the first step the pH of the acidic wastewater is adjusted to an optimum operating pH by the addition of an alkali. The optimum pH is determined by laboratory jar tests and/or pilot tests on the wastewater being tested. Figure 7 shows the effect that solution pH has on metal sulfide solubilities. The most commonly used alkalis are lime or caustic.

Following adjustment of the pH of the stream, the sulfide reagent is added in a flash mix reaction tank. The most commonly used reagents are the soluble sulfides including sodium sulfide, sodium bisulfide, calcium sulfide, and barium sulfide. The reactions occurring between these reagents and the dissolved metal cations forming the metal sulfide precipitates are:

for sodium sulfide -

$$Na_2S \rightleftarrows Na^+ + S^= \qquad (6\text{-}5)$$

$$M^{++} + S^= \rightleftarrows MS\downarrow \qquad (6\text{-}6)$$

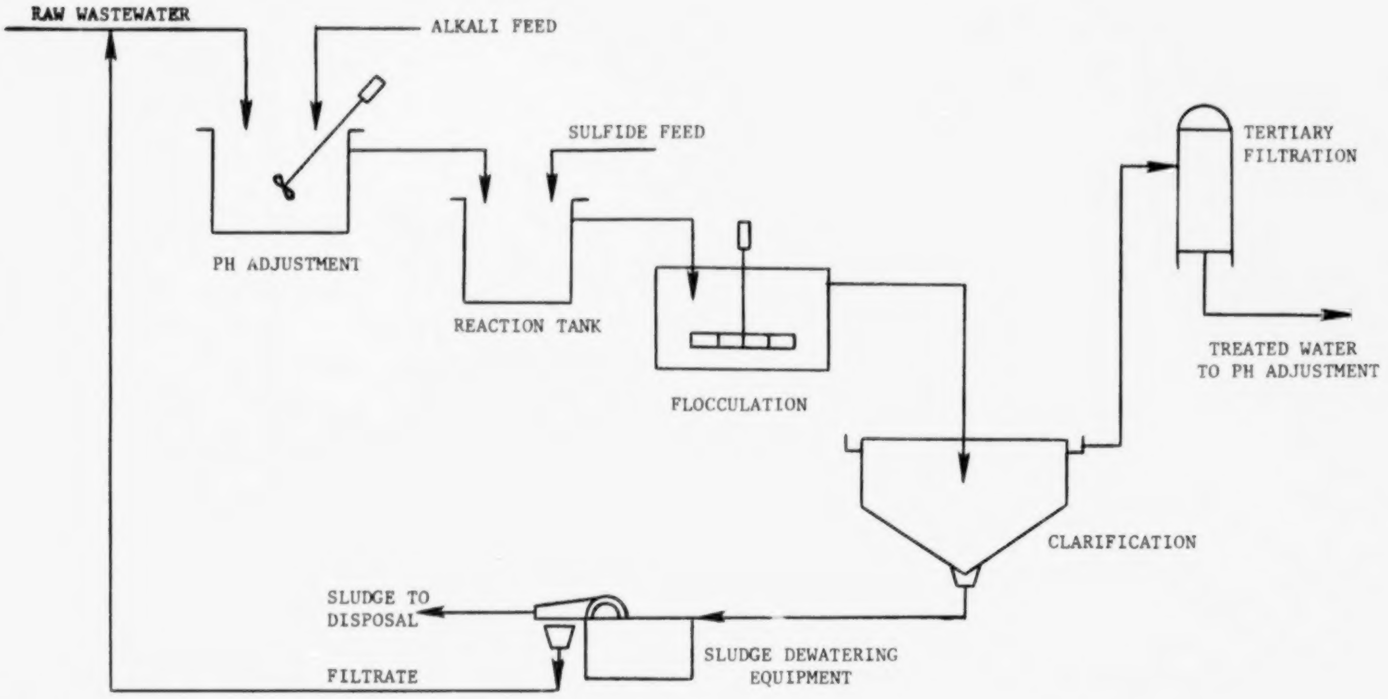
RAW WASTEWATER
ALKALI FEED
PH ADJUSTMENT
SULFIDE FEED
REACTION TANK
FLOCCULATION
TERTIARY FILTRATION
TREATED WATER TO PH ADJUSTMENT
CLARIFICATION
SLUDGE TO DISPOSAL
FILTRATE
SLUDGE DEWATERING EQUIPMENT

Figure 6. Typical continuous flow sulfide precipitation treatment system.

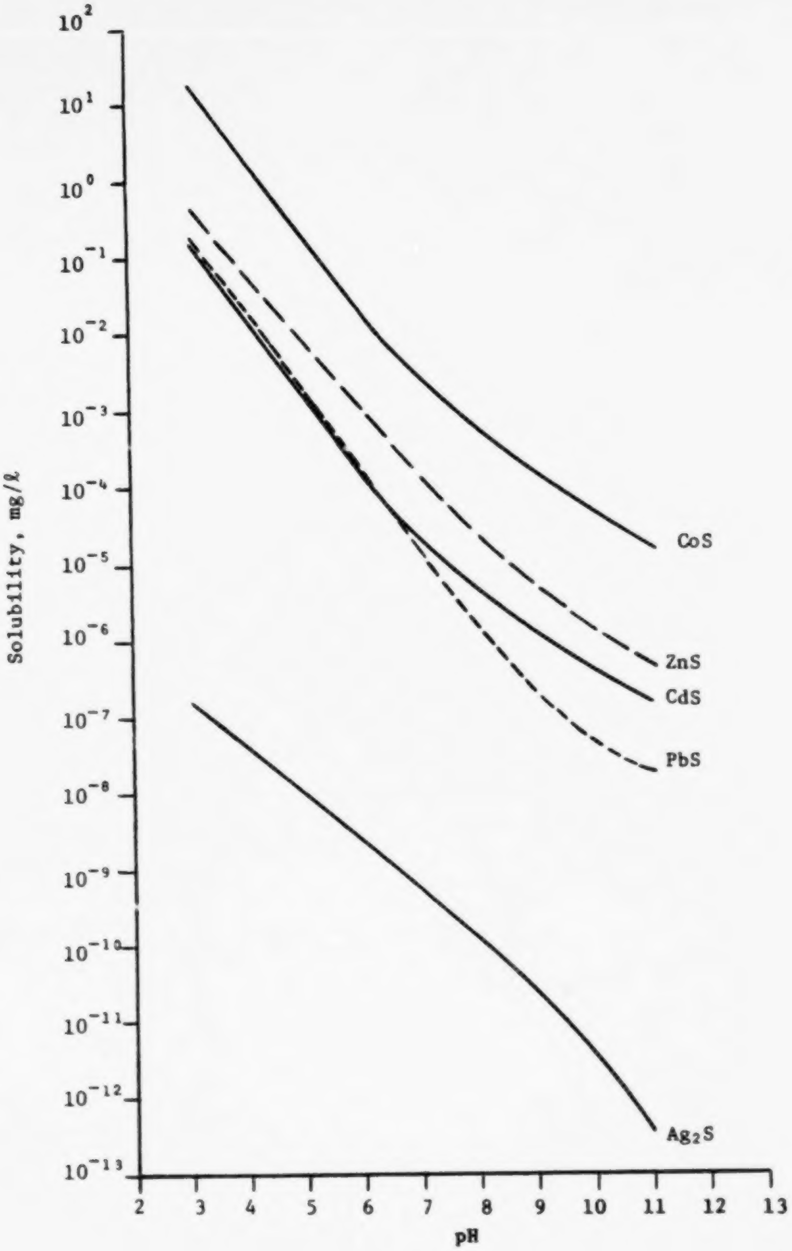

Figure 7. Theoretical solubilities of metal sulfides as a function of pH.

Source: PE-317

for calcium sulfide -

$$CaS \rightleftarrows Ca^{++} + S^{=} \tag{6-7}$$

$$M^{++} + S^{=} \rightleftarrows MS\downarrow \tag{6-8}$$

for sodium bisulfide -

$$NaHS \rightleftarrows Na^{+} + HS^{-} \tag{6-9}$$

$$HS^{-} \rightleftarrows H^{+} + S^{=} \tag{6-10}$$

$$M^{++} + S^{=} \rightleftarrows MS\downarrow \tag{6-11}$$

for barium sulfide -

$$BaS \rightleftarrows Ba^{++} + S^{=} \tag{6-12}$$

$$M^{++} + S^{=} \rightleftarrows MS\downarrow \tag{6-13}$$

where M^{++} is the dissolved metal cation. As with hydroxide precipitation, dosage rates for the sulfide reagent depend upon characteristics of the specific wastewater being treated.

Excess sulfide must be avoided since there is potential for formation of hydrogen sulfide gas. Therefore, it is very important that sulfide dosages be properly controlled in order to effectively remove metals without generating H_2S. Two process control techniques have been used to minimize excess sulfide doses and therefore minimize H_2S formation. The first was used at two pilot plants treating acid mine drainage (LA-326). When the reactions between the sulfide reagent and the dissolved metals are completed, a sharp rise in pH will be observed. This method uses a pH monitor as a feedback control to regulate the sulfide dosage rate.

The second method was used in two applications, one at a copper smelter in Japan to treat sulfuric acid plant blowdown (MU-153), the other at a pilot plant treating photographic developer effluent (LA-337). This method uses an oxidation/reduction potentiometer to monitor the electric potential of the reaction solution. When the precipitation reactions are complete, there is a sharp negative change in the solution potential.

The remaining treatment steps for sulfide precipitation are flocculation, clarification, and final effluent filtration and pH adjustment. These are performed in a similar manner as described earlier for hydroxide precipitation.

An alternative processing scheme to the continuous flow system is batch treatment. The general batch treatment system described under hydroxide precipitation could be used also for sulfide precipitation. Figure 3 shows the flow scheme for a batch treatment facility.

Control Effectiveness

Sulfide precipitation is effective at removing most metals found in acid wastewaters. Among the metal ions reported to be removed are arsenic, cadmium, cobalt, copper, iron, mercury, nickel, and zinc. The chlor-alkali industry uses sulfide to remove mercury from their effluents. Sulfide precipitation is also being applied in the primary copper industry. Table 8 lists reported influent and effluent metal concentrations for sulfide systems treating various wastewater streams. It should be noted that this information is based upon application of sulfide precipitation to various industrial wastewaters. Wastewater characteristics may vary significantly from site to site even within a given industry. These characteristics as well as the design and operation of the precipitation facility will ultimately determine the effectiveness of sulfide precipitation upon metals removal. For this reason, the residual concentrations reported in Table 8 should not be taken as an accurate measure of sulfide's performance in specific applications. Instead these numbers should be interpreted as an indication of the range of removal effectiveness for sulfide precipitation.

TABLE 8. SULFIDE PRECIPITATION METAL REMOVAL EFFECTIVENESS

Metal	Inlet Concentration (mg/ℓ)	Residual Concentration (mg/ℓ)
Arsenic	0.8-132.0	0.05-26.4
Cadmium	0.44-1.0	0.008
Copper	50-115	0.5
Mercury	0.3-50.0	0.01-0.12
Zinc	42	1.16

Source: PA-322

Furukawa Co. Ltd. uses sodium hydrosulfide (NaHS) to treat sulfuric acid plant blowdown at their Ashio copper smelter in Japan (MU-153). This is the only nonferrous smelter which has reported removal efficiencies to date. The data reported are as follows (MU-153):

	Concentration (ppm)	
Metal	Influent	Effluent
As	8,530	0.03
Cu	120	0.05
Pb	30	0.5
Cd	60	0.3

These data are from a batch process. Reaction times are between 2 and 3 hours. A sharp negative change on an oxidation/reduction potentiometer indicates the reaction end point.

It should also be noted, that H_2S is used in the production of primary cobalt. In this industry, the sulfide is used to selectively precipitate iron, copper, zinc and then cobalt and nickel at increasing pH values. Sulfide is used in this process because of its ability to effectively remove the cobalt and other impurities from the leaching liquor.

Energy Requirements

Because of the limited application of sulfide precipitation, information in the literature on the energy usage for a full-scale system was not available. However, since much of the basic processing scheme for sulfide precipitation is the same as that for hydroxide precipitation the primary energy users will probably be similar. The one main exception to this is the energy usage of the sludge dewatering equipment. Sulfide precipitation will probably result in less sludge being generated per volume of wastewater treated. This is because a sulfide system can operate at a lower pH than a hydroxide system and still effectively remove dissolved metals (see Figures 2 and 7). Therefore, less alkali is needed to adjust the pH of the waste stream and less sludge is formed in the flocculator. The size and energy requirement for the sludge handling equipment, therefore, will be lower than for hydroxide precipitation. The energy requirements of 8 kWh to 14 kWh for the hydroxide precipitation system described in the previous section should be representative of the high end of the range of energy requirements for sulfide precipitation.

Economics

As with the energy requirements, estimates for the costs associated with sulfide precipitation were not found in the literature. However, the costs associated with sulfide precipitation may be approximated by those given earlier for hydroxide precipitation. There are several differences in the two systems that should be noted which will affect the capital and operating and maintenance costs for sulfide precipitation, though. Those differences which will probably increase capital costs include:

- a separate reaction tank and associated equipment for sulfide addition,
- hoods on the reaction tank and flocculator/clarifier for H_2S control, and
- special instrumentation to control excess sulfide addition.

There is one difference which will probably lower capital costs:

- smaller sludge handling equipment due to the lower operating pH of the system.

Smaller sludge volumes will result because of the lower operating pH. At lower solution pH values, calcium carbonate will not precipitate as in the hydroxide precipitation system.

With respect to operating cost, the primary difference which will probably increase the sulfide precipitation costs is the expense of the sulfide reagent. Sodium sulfide, for example, costs roughly $275 per ton versus lime costs of $25 per ton and sodium hydroxide costs of $150 per ton. Those differences which will probably lower the costs are:

- less sludge volume to dewater, and
- less lime or sodium hydroxide needed since the operating pH is lower.

Secondary Process Emissions

The two major environmental problems associated with the sulfide precipitation process are the potential generation of hydrogen sulfide (H_2S) gas and the production of a metal sulfide sludge. Hydrogen sulfide formation results from the addition of excess sulfide which reacts with water as shown:

$$2H_2O + S^{=} \rightleftarrows 2OH^{-} + H_2S\uparrow \qquad (6\text{-}14)$$

H_2S formation can be minimized either through operating the system at a pH above 8.0 or by one of the two methods mentioned earlier, i.e., carefully monitoring the solution pH during sulfide addition or monitoring the electrical potential of the reaction solution. As can be seen in Figure 8, at a solution pH above 8.0, hydrogen sulfide will disassociate into HS^- and H^+. Operating at a pH of 8.0 is not desirable for smelters first, because of the additional cost of hydroxide for neutralization and second, because most metals will precipitate as hydroxides. It is preferable to recycle metals in the sludge in the form of sulfides rather than hydroxides. Sulfides are the normal feed to a smelting furnace. Metal hydroxides require more energy to smelt and are likely to be lost in the smelting furnace slags. Therefore, it is believed that the optimum pH for a sulfide system may be as low as 4 to 5. As a result, the other control measures were developed to minimize H_2S liberation. As an additional control, ventilation is normally provided on all of the reaction equipment.

Metal sulfide sludge disposal is the other major environmental problem associated with sulfide precipitation processes. There are several disposal alternatives which have been investigated. These include:

- maintaining the sludge in an oxygen free environment (SC-A-503).
- chemical treatment or fixation (EN-394), and
- recycling the sludge to a smelter for metals recovery (MU-153, CO-A-683).

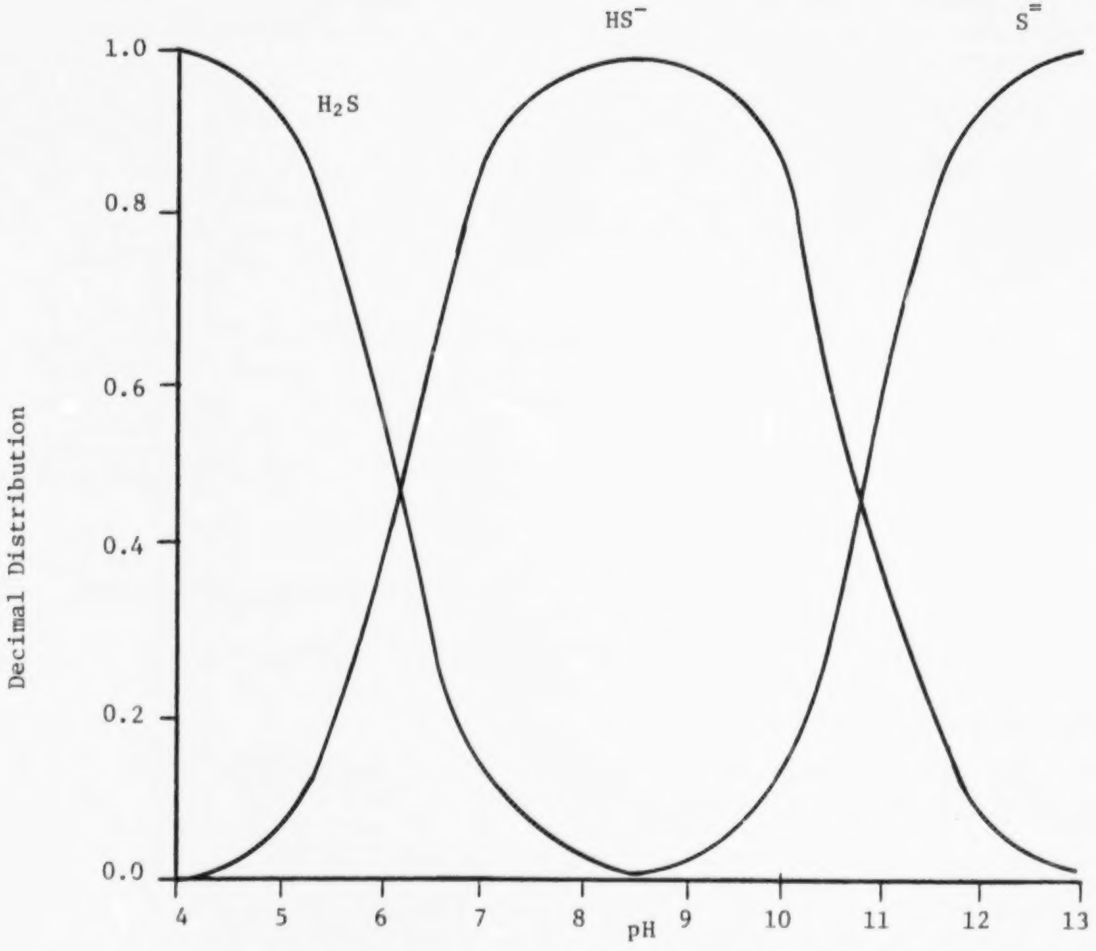

Figure 8. Distribution of hydrogen sulfide species as a function of pH.

Source: WA-A-356

If metal sulfide sludges are placed in a typical landfill, exposure to air can oxidize the sulfide portion and eventually create an acid environment. As the pH decreases the heavy metals portion can dissolve and be leached from the site back into the environment via surface runoff or percolation through the soil mantle with subsequent groundwater contamination.

Probably the most practical and least expensive disposal technique for the nonferrous metals smelting industry is recycle of the sludge for recovery of the metals. A smelting plant in Sweden has installed a sodium sulfide wastewater treatment facility which will recycle recovered sludge back to its copper roasters for disposal.

ION EXCHANGE

Ion exchange is a process in which mobile ions of one phase are exchanged for ions of the same charge in another phase. Although the most common ion exchange systems consist primarily of a solid phase with a surrounding liquid phase, some specialized applications employ two immiscible liquid phases.

Although the process was first discovered in 1848, the first successful application occurred almost sixty years later for the purpose of water softening. While this is still the most common application, the recent demand for ultrapure water by electric power utilities and transistor and microcircuit industries has resulted in many improvements in ion exchange systems. Currently ion exchange technology is being used in the following industries:

- metals plating,
- pharmaceuticals processing,
- heavy metals (cobalt, nickel, copper, molybdenum, and vanadium) recovery and purification, and
- boiler feedwater pretreatment in many industries.

Process Description

The basic mechanism of ion exchange involves the reversible interchange of similarly charged ions in separate phases, usually a solid resin immersed in a liquid medium. Ion exchange resins are the heart of the ion exchange process. These resins may be either strongly acidic, weakly acidic, strongly basic, or weakly basic, depending on groups attached at the surface. A strongly acidic resin will contain functional groups derived from a strong acid such as H_2SO_4, whereas, a weakly acidic resin will be derived from a weak acid such H_2CO_3. Basic resins that contain functional groups derived from weak base amines ($R-NH_2$, $R-R'NH$, and $R-R'_2N$) are termed weakly basic, while those resulting from quaternary ammonium compounds ($R-R'_3N^+OH^-$) are considered strongly basic. Table 9 presents representative ion exchange reactions and appropriate regenerants for the four different exchange resins (WE-324).

TABLE 9. TYPICAL REACTIONS FOR ION EXCHANGE RESINS

Strongly Acidic Cation Exchangers.

a. Hydrogen form, regenerate with HCl or H_2SO_4.

$$2(R - SO_3H) + Ca^{2+} \rightleftarrows (R\text{-}SO_3)_2Ca + 2H^+ \tag{6-15}$$

b. Sodium form, regenerate with NaCl.

$$2(R - SO_3Na) + Ca^{2+} \rightleftarrows (R\text{-}SO_3)_2Ca + 2Na^+ \tag{6-16}$$

Weakly Acidic Cation Exchanger.

a. Hydrogen form, regenerate with HCl or H_2SO_4.

$$2(R - COOH) + Ca^{2+} \rightleftarrows (R - COO)_2Ca + 2H^+ \tag{6-17}$$

b. Sodium form, regenerate with NaOH.

$$2(R - COONa) + Ca^{2+} \rightleftarrows (R - COO)_2Ca + 2Na^+ \tag{6-18}$$

Strongly Basic Anion Exchanger.

a. Hydroxide form, regenerate with NaOH.

$$2(R - R'_3NOH) + SO_4^{2-} \rightleftarrows (R - R'_3N)_2SO_4 + 2OH^- \tag{6-19}$$

b. Chloride form, regenerate with NaCl or HCl.

$$2(R - R'_3NCl) + SO_4^{2-} \rightleftarrows (R - R'_3N)_2SO_4 + 2Cl^- \tag{6-20}$$

Weakly Basic Anion Exchanger.

a. Free base or hydroxide form, regenerate with NaOH, NH_4OH, or Na_2CO_3.

$$2(R - NH_3OH) + SO_4^{2-} \rightleftarrows (R - NH_3)_2SO_4 + 2OH^- \tag{6-21}$$

b. Chloride form, regenerate with HCl.

$$2(R - NH_3Cl) + SO_4^{2-} \rightleftarrows (R - NH_3)_2SO_4 + 2Cl^- \tag{6-22}$$

Source: WE-324

For water and wastewater treatment there are two principal methods for applying ion exchange, batch and fixed bed. In batch operation a predetermined quantity of ion exchange resin is added to a specified volume of water and mixed until the exchange reaction attains equilibrium. Normally batch operation is considered inefficient because only a fractional amount of the total resin capacity is used. However, batch operation has been effective in circumstances where the selectivity of the resin for the ion being removed is very high or when the ion being released by the resin is concurrently removed from the solution being treated. For instance, if the released ion is precipitated from solution, batch operation may be more effective than fixed bed operation.

Fixed bed or column operation is preferred for most applications. Each column is equipped with top and bottom liquid distributors or collectors. Usually a porous bed of gravel or anthracite or a screen is placed in the bottom of the column to support the exchange resin which is loaded approximately halfway to the top. Generally fixed bed operation follows a four step cycle:

- service,
- backwash,
- regeneration, and
- rinse.

During the service step the solution being treated is introduced at the top of the column and allowed to trickle down through the resin bed to be removed by a collector system at the bottom. As the solution is fed into the column, a rather narrow exchange zone will be established where the contaminant ions are being exchanged with the counter ions of the resin. With continued operation the exchange zone will slowly travel downward through the bed leaving exhausted resin behind. When the exchange zone eventually reaches the bottom of the bed, breakthrough of the contaminant ions will occur and the exhausted bed will require regeneration. The amount of operational time before bed regeneration depends on the feedrate and composition of the solution and the size of the column. For manual operation, columns are normally sized to provide a service period of 24 hours in order to reduce labor costs. If the column is on automatic control then the service period may be shortened to four to eight hours in order to reduce equipment size and cost.

Following exhaustion, the resin bed is backwashed to remove fine suspended particles that may have filtered out on the resin. Treated water is introduced through a distributor in the bottom at a high enough flow rate to expand the bed about 75 to 100 percent of its original volume. Although fine particles are carried out through the top collector, the ion exchange resin is not lost. Backflushing will usually last 15 to 30 minutes, after which the resin bed settles to a uniform packing. Any flow channels that may have been formed during the service step are effectively removed by backflushing.

Regeneration is the third step in the cycle and may be accomplished by the introduction of a suitable acid, alkali, or neutral salt. Although regeneration may use either downflow or upflow operation, the latter is usually preferred. With downflow regeneration the very bottom of the bed is not fully regenerated and subsequent service operation will cause contaminant leakage. If upflow regeneration is used, the partly regenerated resin is at the top of the bed and subsequent service operation will only displace the contaminant deeper into the bed rather than out with the product. In addition, upflow regeneration is immediately effective since the contaminants released from the lower bed portion are flushed through the complete exhausted upper bed volume where the possibility of removal is negligible. Therefore, a reduction in the regenerant, rinse, and backwash consumption is achieved, which results in a decrease in the amount of regenerant waste. This final point, in reference to regenerant waste, is very important. All ion exchange systems will generate a waste stream which requires proper disposal. If the amount of this waste stream can be reduced, disposal will be simpler and more economic. In some cases, if the contaminant concentration is high enough, recycling of the regenerant waste or further processing for contaminant recovery may be economically attractive.

In the rinse step, treated water is very slowly passed through the bed to displace the remaining regenerant solution. This is followed by a second, faster rinse to flush residual regenerant and displaced ions to waste. The rinse water can be collected and used for regeneration in the next operating cycle. When a predetermined volume or conductivity is reached, the cycle is ready to be repeated beginning with the service step.

Some ion exchange systems designed for the production of deionized water incorporate both acidic (cationic) and basic (anionic) resins in a single column. This mixed-bed treatment has resulted in deionized water of a better quality than in a two column system. The operating cycle is basically the same. A downflow service operation is continued until bed exhaustion. Then an upflow backwash step is used to separate the lighter anion resin particles from the heavier cation resin particles. For regeneration, an acid is fed up through the cation resin and an alkali is fed down through the anion resin. The waste regenerant is drawn off at a zone where the two resins meet. The resin bed is then completely rinsed and compressed air is used to fluidize the system and remix the resins. The operating cycle is again ready to be repeated. The entire cycle is shown in Figure 9.

Control Effectiveness

Ion exchange has an excellent record of performance in wastewater treatment. Several metals, including copper, lead, nickel, and zinc, have been removed to levels lower than 0.4 mg/ℓ. Table 10 presents the influent and effluent concentrations of several heavy metals in water streams treated by ion exchange processes. This information is not directly based upon the application of ion exchange to primary nonferrous industry wastewaters.

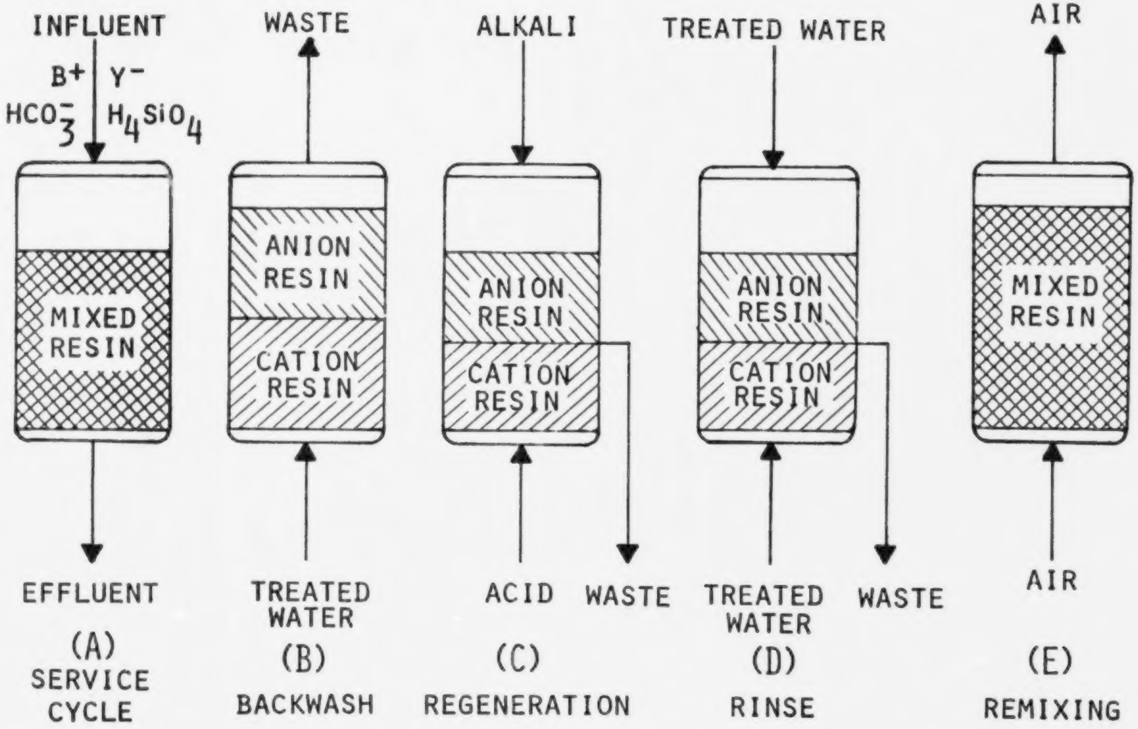
INFLUENT
B^+
Y^-
HCO_3^-
H_4SiO_4
MIXED RESIN
EFFLUENT
(A)
SERVICE CYCLE
WASTE
ANION RESIN
CATION RESIN
TREATED WATER
(B)
BACKWASH
ALKALI
ANION RESIN
CATION RESIN
ACID
WASTE
(C)
REGENERATION
TREATED WATER
ANION RESIN
CATION RESIN
TREATED WATER
WASTE
(D)
RINSE
AIR
MIXED RESIN
AIR
(E)
REMIXING

Figure 9. Operating cycle for mixed-bed ion exchange system.

TABLE 10. ION EXCHANGE METAL CONTROL EFFECTIVENESS

Metal	Inlet Concentration (mg/ℓ)	Effluent Concentration (mg/ℓ)
Cadmium	0.1	0.001
Chromium, hexavalent	8-10.7	0.0-0.9
Copper	1.02	0.03
Lead	0.055-144.8[1]	0.0015-0.53[1]
Manganese	50[1]	0.046[1]
Mercury	1.4-2.8	0.005
Nickel	150-900	0.01
Zinc	6	0.4

[1] Pilot plant test data.

Source: PA-120

The control effectiveness of a particular ion exchange resin for a specific contaminant is determined by the ion selectivity of that resin. The ion selectivity, in turn, is determined by a number of factors including solution concentration of the ion, valence of the ion, temperature, pressure, ion pair formation, structure of the exchange resin, and precipitate formation. All of these factors are well discussed in literature (SA-136 and WE-324).. Table 11 summarizes the order of selectivity for various ions with various exchangers (CE-034).

TABLE 11. SELECTIVITY ORDER FOR VARIOUS IONS WITH VARIOUS EXCHANGERS

I. Strong Acid Cation Exchanger (8% Crosslinking).

$Ba^{++} > Pb^{++} > Hg^{++} > Cu^{+} > Sr^{++} > Ca^{++} > Ni^{++} > Cd^{++} > Cu^{++} > Co^{++} > Zn^{++} \simeq Cs^{+} > Rb^{+} > Fe^{++}$
$> Mg^{++} \simeq K^{+} > Mn^{++} > NH_4^{+} > Na^{+} > H^{+} > Li^{+}$

II. Weak Acid Cation Exchanger (Carboxylic).

$H^{+} > Cu^{++} > Co^{++} > Ni^{++} > Ca^{++} > Mg^{++} > Na^{+}$

III. Strong Base Anion Exchanger.

Type I: Benzene sulfonate > salicylate > citrate > I^{-} > Phenate > $HSO_4^{-} > ClO_3^{=} > NO_3^{-} > Br^{-}$
$CN^{-} > HSO_3^{=} > BrO_3^{-} > NO_2^{-} > Cl^{-} > HCO_3^{-} > IO_3^{-}$ > Formate > Acetate > Propionate > $F^{-} > OH^{-}$

Type II: Nearly the same except iodide is less that phenate and hydroxide is after bicarbonate.

IV. Weak Base Anion Exchanger.

$OH^{-} > SO_4^{=} > CrO_4^{=} > AsO_4^{=} > PO_4^{=} > MoO_4^{=} > Cl^{-}$

V. Chelate Resin (Dowex A-1).

$Pd^{++} > Cu^{++} > Fe^{++} > Ni^{++} > Pb^{++} > Mn^{++} > Ca^{++} > Mg^{++} > Na^{+}$

Source: CE-034

Energy Requirements

The only energy required for ion exchange treatment is for pumping. The average energy requirement is approximately 1.1 kWh per 1000 gallons of water treated (MA-693). This estimate is independent of the concentration of total dissolved solids in the feed water.

Economics

Ion exchange is very unique in that the costs of this treatment per unit volume of water decrease with a decrease in the concentration of the metal ion. This makes ion exchange a very attractive means for treating wastewater streams with metals concentrations less than 200 mg/ℓ. Some recently developed resins, which have improved selectivities for particular metal ions, may increase the concentration level at which ion exchange systems are economically attractive. In cases where a reduction in dissolved solids is of primary importance, ion exchange is considered economically practical if the solids concentration is less than 1,000 mg/ℓ. For solids concentrations greater than 1,000 mg/ℓ, processes such as reverse osmosis and electrodialysis are usually more economical than ion exchange (WE-324).

The capital and operating costs for an ion exchange system can vary depending on the volume and composition of the stream being treated. The principal operating cost is regeneration and is highly dependent on the ion exchange resins employed, the raw water quality, and the operating arrangement. Strongly basic resins will involve higher operating costs than weakly basic resins because of the regenerant required. Strongly basic resins are regenerated by solutions of sodium hydroxide, which may cost from 8 to 16 cents per pound (VE-074). Regeneration of strongly basic resins is also less efficient than for weakly basic resins. Estimated operating costs for weakly basic resins is on the order of fifteen cents per thousand gallons per gram per gallon removed (WE-324). In almost every instance, ion exchange systems are tailored to the specific installation and its wastewater, so that general economic data is incomplete. Table 12 presents the economics of several ion exchange systems based on system capacity and dissolved solids concentration.

Secondary Process Emissions

The treatment of any waste stream by ion exchange results in resin regeneration wastes. These wastes contain the pollutants removed from the effluent stream that is treated. The pollutants are concentrated in the acidic or basic regeneration solution. The two solutions are usually combined for neutralization. Further treatment of these wastes is required prior to their discharge.

TABLE 12. ECONOMICS OF ION EXCHANGE WATER TREATEMENT (1977)

System Capacity (10^3 gal/day)	25	25	25	100	100	100	500	500	500	7,200
Dissolved Solids Concentration (ppm)	100	200	500	100	200	500	100	200	500	20
Installed Capital Cost (10^3 \$)	68	70	73	145	170	174	275	275	275	1,700
Operating Costs (\$/1000 gal)										
Capital Service	0.92	0.94	0.99	0.51	0.54	0.58	0.18	0.18	0.18	
Chemical (Regeneration and Waste, including Water)	0.24	0.48	1.20	0.24	0.49	1.22	0.28	0.56	1.40	
Resin Replacement	0.05	0.05	0.05	0.06	0.06	0.06	0.07	0.07	0.07	
Power (@ \$0.035/kWh)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	
Labor (@ \$10/hr)	0.15	0.15	0.15	0.10	0.10	0.10	0.05	0.05	0.05	
Maintenance and Repairs	0.10	0.10	0.10	0.08	0.08	0.08	0.05	0.05	0.05	
Total Operating Cost (\$/1000 gal)	1.50	1.76	2.53	1.03	1.31	2.08	0.67	0.95	1.79	0.10
Yearly Operating Cost (10^3 \$)*	13	15	22	36	46	73	117	166	313	250

* Assumed operating schedule 85% service - 350 days/yr.
Sources: DI-150, MA-693

In addition, a resin bed will eventually require complete replacement when it can no longer be sufficiently regenerated. The spent resin becomes a solid waste and is usually disposed of by landfilling.

REVERSE OSMOSIS

Reverse osmosis (RO) is a process designed to purify contaminated streams by forcing water through a semipermeable membrane. The membrane will readily allow the passage of water under pressure, but prevents the transport of contaminants. The result of wastewater treatment by reverse osmosis is a pure water product stream and a highly concentrated reject stream.

Undoubtedly the most widespread use of reverse osmosis systems has been the desalinization of water. Since the early 1970's, however, reverse osmosis has been commercially used to treat wastewater streams from a number of industries including:

- electroplating,
- printed circuit board manufacturing,
- acid battery manufacturing,
- metal finishing (such as nickel plating), and
- ore mining.

In some cases, treatment by reverse osmosis resulted in a high volume product stream of environmentally acceptable quality and a low volume, highly concentrated reject stream which required additional treatment before final disposal. In other cases, reverse osmosis was able to provide process makeup water from the product stream and valuable mineral recovery from the reject stream. Therefore, for a stream containing heavy metals, reverse osmosis can be used to concentrate the metals in a lower volume stream for additional treatment and final disposal or for metals recovery. For smelter wastewaters, however, filtering would be required as a pretreatment step in order to prevent clogging of the filter membrane.

Process Description

Osmosis is the flow of water from a dilute solution through a semipermeable membrane to a more concentrated solution. The driving force is referred to as osmotic pressure. When a pressure greater than the osmotic pressure is applied to the concentrated solution, the process can be reversed. Water will pass from the concentrated solution through the membrane, leaving dissolved species in the concentrated solution. Once the osmotic pressure is exceeded, the rate of flow through the membrane is roughly proportional to the applied pressure (WI-316).

Reverse osmosis should not be confused with ultrafiltration. Since reverse osmosis uses a "tighter" membrane and operates at considerably higher pressures (400-1,000 psi) than ultrafiltration, it is capable of rejecting dissolved electrolytes and organics of much lower molecular weight.

A schematic flow diagram of a typical reverse osmosis plant is presented in Figure 10. The system consists basically of high pressure process pumps that supply feed to a number of reverse osmosis modules connected either in series or parallel. If the reverse osmosis modules are arranged in series, the feed, in effect, will undergo treatment a number of times and a higher quality product can be achieved. In some cases, the reject stream may be recycled to the feed stream or fed directly to another RO module to reduce the volume or increase the concentration for further treatment. Such recycling or series treatment of the reject stream may be limited by the ability of the membrane to withstand concentrated contaminants. If the product quality is not critical, then the modules can be arranged in parallel to provide high system capacity.

The plant must also have some feed pretreatment equipment, usually some form of pH adjustment and filtration, to prevent membrane damage. Most commercially available membranes can withstand feed streams with a pH between 2.5 and 11, although the most commonly recommended pH is moderately low (4 to 7). In addition, the feed should have a low solids loading to prevent the membrane from becoming plugged.

While reverse osmosis systems are designed for specific applications, operating conditions can vary considerably depending on the feed stream to be processed, the quality of product desired, and the type of membrane material employed. Typical operating pressures may range from 200 to 1000 psi, while temperatures may vary from 55 to 95°F. Within this range a reverse osmosis unit can generally be operated to produce anywhere from 50 to 90 percent of the total feed volume as product.

A variety of semipermeable membranes have been used in reverse osmosis units. In the past the most popular membrane material has been cellulose acetate (GI-019). The membrane was designed to be approximately 100 microns thick. Of this thickness less than 1 percent was composed of the dense skin which exhibits the semipermeability required for reverse osmosis membranes. The remaining portion of the cellulose consisted of a porous substrate that provided the membrane with structural strength (LY-006).

Recently, however, aromatic polyamide membranes have received more attention due to their ability to treat a wider range of contaminated feeds. For example, one manufacturer produces a polyamide membrane which can be operated at temperatures up to 95°F (@ 800 psi), pressures up to 1000 psi (@ 77°F), and over a pH range of 4 to 11 (TE-361, RA-579). Two other very promising membrane materials are a nonpolysaccharide polymer (RO-389) and a polybenzimidazolone (NE-314). The nonpolysaccharide membrane has been experimentally used in treating metal finishing wastewaters with a pH range of 0.5 to 12.9 and has shown no significant signs of deterioration (RO-389). The polybenzimidazolone membrane was primarily developed for use in water desalting and has been experimentally shown to handle a pH range of 1 to 12, resist oxidation by chromic acid, and withstand temperatures up to 140°F (NE-314).

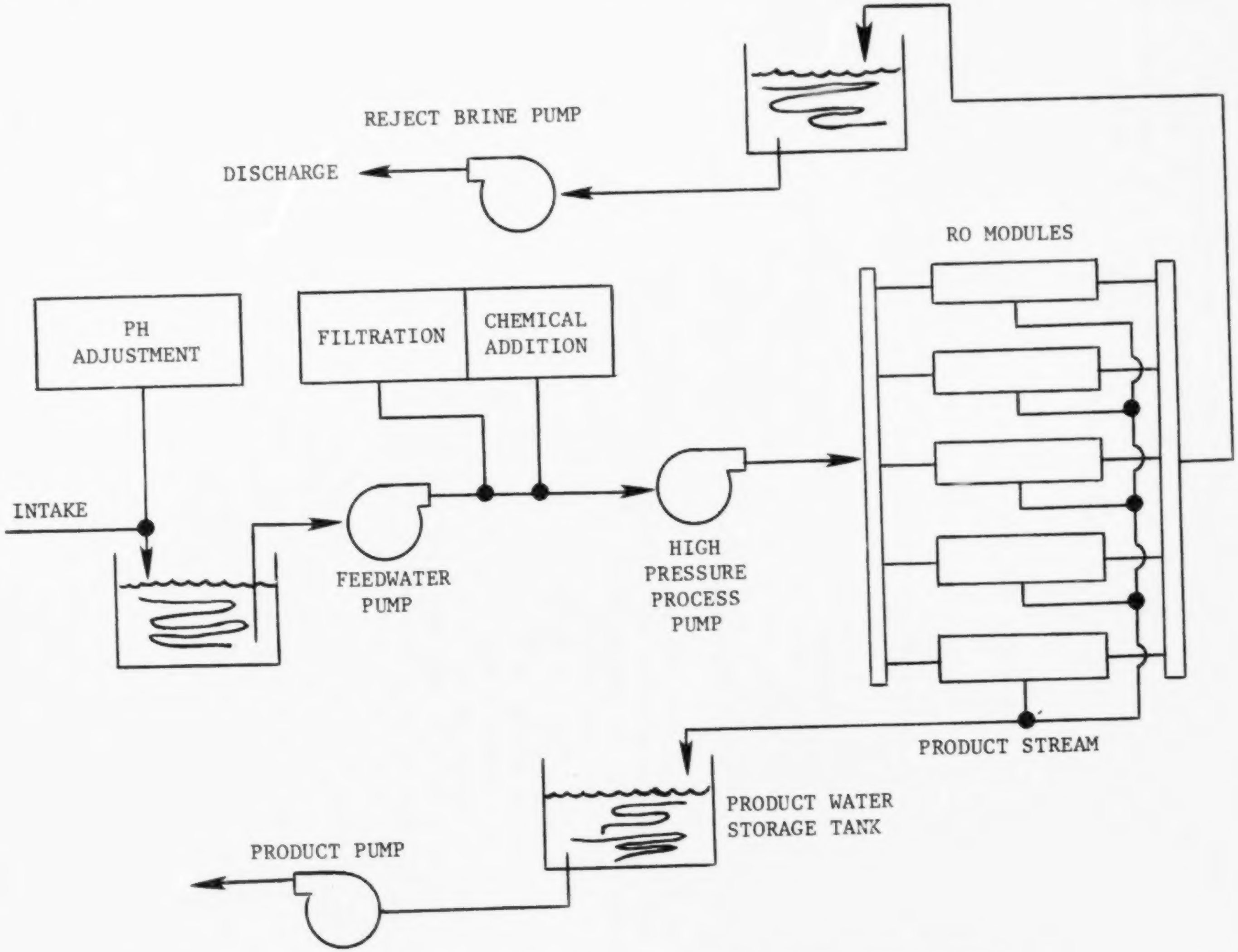
REJECT BRINE PUMP
DISCHARGE
RO MODULES
PH ADJUSTMENT
FILTRATION
CHEMICAL ADDITION
INTAKE
FEEDWATER PUMP
HIGH PRESSURE PROCESS PUMP
PRODUCT STREAM
PRODUCT WATER STORAGE TANK
PRODUCT PUMP

Figure 10. Typical reverse osmosis plant arrangement.

Source: HI-041

In addition to the variety of available membrane materials, there are also several possible membrane configurations. For reverse osmosis systems, the term configuration refers to the membrane supporting mechanism. Early reverse osmosis systems relied on relatively simple configurations, such as plate and frame or tubular membranes. Newer systems are employing either spiral wound or hollow fiber membranes, primarily because of the increased membrane surface area and good structural strength. Figure 11 shows the hollow fiber configuration.

Control Effectiveness

The control effectiveness for reverse osmosis units can vary considerably depending on the feed characteristics, pretreatment, and desired conversion. The conversion for a particular RO system is the percent of feed recovered as product. For example, if a reverse osmosis unit was producing 7 gpm of pure water from a 10 gpm feed stream, the conversion would be 70 percent.

The control effectiveness is often reported as the percent rejection for a particular contaminant, where the rejection is defined as the ratio of the difference between the feed and product concentrations to the feed concentration (feed concentration-product concentration/feed concentration). A rejection of 100 percent would signify complete contaminant removal.

At 70 percent conversion single stage reverse osmosis units have typically demonstrated 90 to 98 percent rejection for dissolved solids. Multiple stage RO units can be used to achieve even higher conversion and better product quality. Reverse osmosis can also remove more than 95 percent of most organics and all colloidal particles down to 0.05 microns (DI-149). Table 13 presents typical rejections and concentrations of feed and product streams for RO treatment of streams containing some metals. The data reveal that heavy metal ions are removed at least 99 percent. Other tests indicate that copper is also rejected at the same level (WI-316). The effectiveness of zinc removal by RO is not nearly as conclusive. One source considers RO an attractive system for zinc removal (SK-049), while another regards RO as unsatisfactory (PA-120).

Energy Requirements

The major power consumer in a reverse osmosis unit is the pumps. For 100,000 gpd units and larger, the energy requirements are between 8 and 10 kWh/1000 gallons of water processed for one stage. If multiple stage reverse osmosis processes are used, the energy requirements will increase almost directly with the number of stages.

Economics

The economics of RO treatment systems are very site-specific and will depend on feed stream characteristics, required pretreatment, desired product conversion and quality, and ultimate disposal of the reject stream. Major factors influencing capital cost are the feedwater rate and the number of

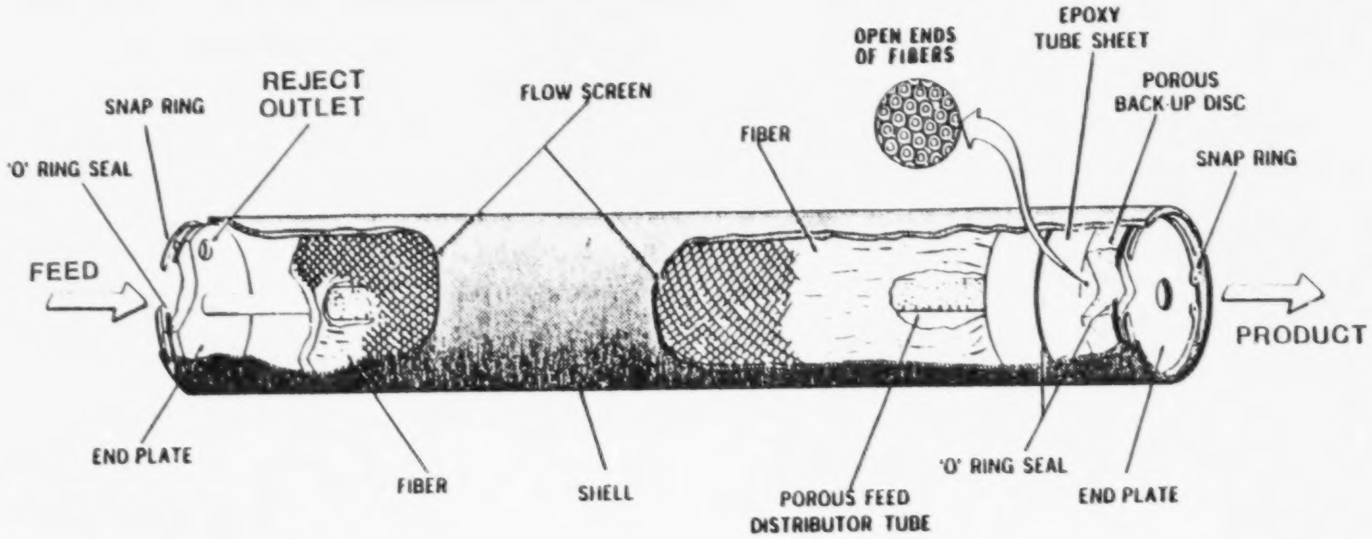
'O' RING SEAL
SNAP RING
REJECT OUTLET
FEED
FLOW SCREEN
FIBER
OPEN ENDS OF FIBERS
EPOXY TUBE SHEET
POROUS BACK-UP DISC
SNAP RING
PRODUCT
END PLATE
FIBER
SHELL
POROUS FEED DISTRIBUTOR TUBE
'O' RING SEAL
END PLATE

Figure 11. Cut away drawing of hollow fiber RO system.

Source: MA-392

TABLE 13. TYPICAL REJECTIONS BY REVERSE OSMOSIS SYSTEMS[1]

Systems	pH	Cond.[2]	Acidity	Ca	Mg	Total Fe	Fe II	Al	SO_4	Mn
SPIRAL WOUND[3]										
Feed Water	3.1	2070	460	260	170	77	64	12	1340	43
Product	4.4	17	38	0.4	0.3	0.4	0.3	0.2	0.9	0.5
Rejection (%)[4]	---	99.2	91.7	99.8	99.8	99.8	99.8	99.2	99.9	98.8
TUBULAR										
Feed Water	3.4	1050	250	125	92	78	61	12	660	14
Product	4.2	46	46	2.2	1.4	0.9	1.0	1.0	4.4	0.3
Rejection (%)[4]	---	95.6	81.6	98.2	98.5	98.8	98.4	91.7	99.3	97.8
HOLLOW FIBER										
Feed Water	3.4	1020	210	150	115	110	71	15	940	14
Product	4.3	32	32	1.2	1.4	1.2	0.8	0.8	4.6	0.1
Rejection (%)[4]	---	96.9	84.8	99.2	98.8	98.9	98.9	94.7	99.5	99.1

[1] All units are mg/ℓ except pH.

[2] Cond.-Specific conductance (micromhos/cm).

[3] 75 percent conversion.

[4] Rejection = 100 (Feed concentration - Product concentration)/Feed concentration.

Source: WI-316

stages employed. Operating costs will depend on a number of variables including labor, power, maintenance, chemical pretreatment, and membrane replacement costs. Table 14 presents some typical costs of water treatment by reverse osmosis. Depending on system capacity, capital costs range from \$0.73 to \$2.00 per gallon per day of capacity and operating costs may be \$0.66 to \$2.18 per gallon treated. These costs were not specifically derived from acid wastewater treatment data.

Secondary Process Emissions

Reverse osmosis is a unit operation that requires integration with other wastewater treatment processes. Not only must all feeds to an RO unit be pretreated to some extent, but the reject stream, which contains concentrated contaminants, must also be treated for proper disposal. The major waste stream from a reverse osmosis unit is the reject brine stream. This stream carries the majority of the dissolved solids brought into the process by the feedstream. This reject brine stream can be a large volume waste stream (∿25 percent of the original stream). Therefore, reverse osmosis cannot be considered an end-of-pipe treatment. Reverse osmosis is an attractive means of reducing the volume of a waste stream and concentrating contaminant species in order to make other controls more effective and less expensive. It is expected, however, that extensive pretreatment would be required before smelter wastewaters could be treated by reverse osmosis thus eliminating any cost effectiveness of this process.

EVAPORATION PONDS

Evaporation ponds use solar energy to evaporate water from plant waste streams and thus, collect and concentrate dissolved solids and metals. No water streams are taken from the ponds and therefore "zero-discharge" of effluents from a plant is accomplished. The precipitated solids may be allowed to remain on the bottom of the pond or be removed by periodic dredging.

Evaporation ponds have been used throughout the chemical and electric utility industry. Their application is limited primarily by land availability and cost, net annual evaporation rates, and stream flow rate.

Process Description

Evaporation ponds require a very simple arrangement for dealing with acid wastewaters. The wastewater streams are pumped to the pond site and discharged into a single pond or a series of ponds. The water evaporates and dissolved solids in the waste streams as well as other pollutants are collected and contained within the pond. The pond or ponds may be lined to prevent seepage of the wastewater into underground water supplies.

The area required for a single evaporation pond which evaporates G gallons per minute is given by the equation:

$$\text{Area (acres)} = \frac{19.5\ G}{V} \qquad (6\text{-}23)$$

TABLE 14. COST OF WATER TREATMENT BY REVERSE OSMOSIS

System Capacity[1]	10,000 GPD	25,000 GPD	100,000 GPD	500,000 GPD
Capital Cost (Installed)	\$20,000	\$39,900	\$91,000	\$365,000
Membrane Cost	2,200	5,500	22,000	110,000
Operating Costs (\$/1000 gal)				
Membrane Replacement[2]	0.25	0.25	0.25	0.25
Power (@ \$0.02/kWh)	0.34	0.27	0.18	0.17
Labor (@ \$10/hr)	1.28	0.51	0.14	0.07
Maintenance and Repairs	0.15	0.12	0.10	0.08
Chemicals and Filters	0.12	0.10	0.08	0.05
Wastewater[3] Disposal	0.04	0.04	0.04	0.04
TOTAL OPERATING COST (\$/1000 gal)	\$2.18	\$1.29	\$0.79	\$0.66

[1] Assumed Operating Schedule: 85% Service - 350 Days/Year.

[2] Assumed 125% Membrane Replacement every three years.

[3] At 80% Fractional Recovery and Water Cost of \$53/Acre-Foot.

Source: MA-693

where V is the effective net annual evaporation rate (inches/year). The effective evaporation rate for a given location is calculated by subtracting the yearly rainfall from the gross evaporation rate. The resulting number which is based on pure water is the net evaporation rate. The contaminated water in an evaporation pond, however, will not evaporate as fast as pure water. This is due to the reduction in vapor pressure of the pond water caused by the waters dissolved solids. The actual or effective evaporation rate is less, therefore, than the net rate. The effective rate is in the range of 50 to 70 percent of the net rate (FO-130). For geographical areas with net annual evaporation rates less than 20 inches, evaporation ponds are not economical because of resulting large land requirements.

Control Effectiveness

An evaporation pond will provide complete control of a waste stream since no water is discharged from the pond. However, the possibility exists that pond water may seep into the soil below the pond and reach underground water supplies. Liners are installed in ponds to help prevent this, but over a period of time these may occasionally crack or rupture allowing seepage to occur.

Energy Requirements

The energy requirement for operating evaporation ponds comes solely from the energy needed to pump the wastewater to the pond. This requirement will vary significantly depending primarily upon the distance and height change from the wastewater source in the plant to the pond. As an example, for a layout where the wastewater is pumped 1000 feet on level ground, the energy requirement is 0.5 kWh/1000 gallons of wastewater.

Economics

In Figures 12 and 13, capital and operating costs of evaporation ponds are shown as a function of water rate to the pond with the effective net evaporation rate as a parameter. The capital cost is based on a $2/cubic yard figure for land moved to form a 4 foot high dike with a 27 foot base. It is also assumed that the pond liner costs $\$0.25/ft^2$ and land costs $1000/acre. The cost of excavation ranges from $2 to $6/cubic yard depending upon the type of land to be excavated. Liner costs range from $0.20 to $\$0.40/ft^2$ depending upon the type and thickness of liner used. Land costs can range anywhere from $200/acre to $10,000/acre or more. The operating costs are for pumping and dike area maintenance.

As an example of the cost breakdown, consider a 150 gpm ash pond overflow rate for a utility located in a region where the effective net evaporation rate is 30 inches/year. From Equation 6-23, the pond area required to evaporate 150 gpm is 97.5 acres. The installed capital cost of this evaporation pond (1977 dollars) is:

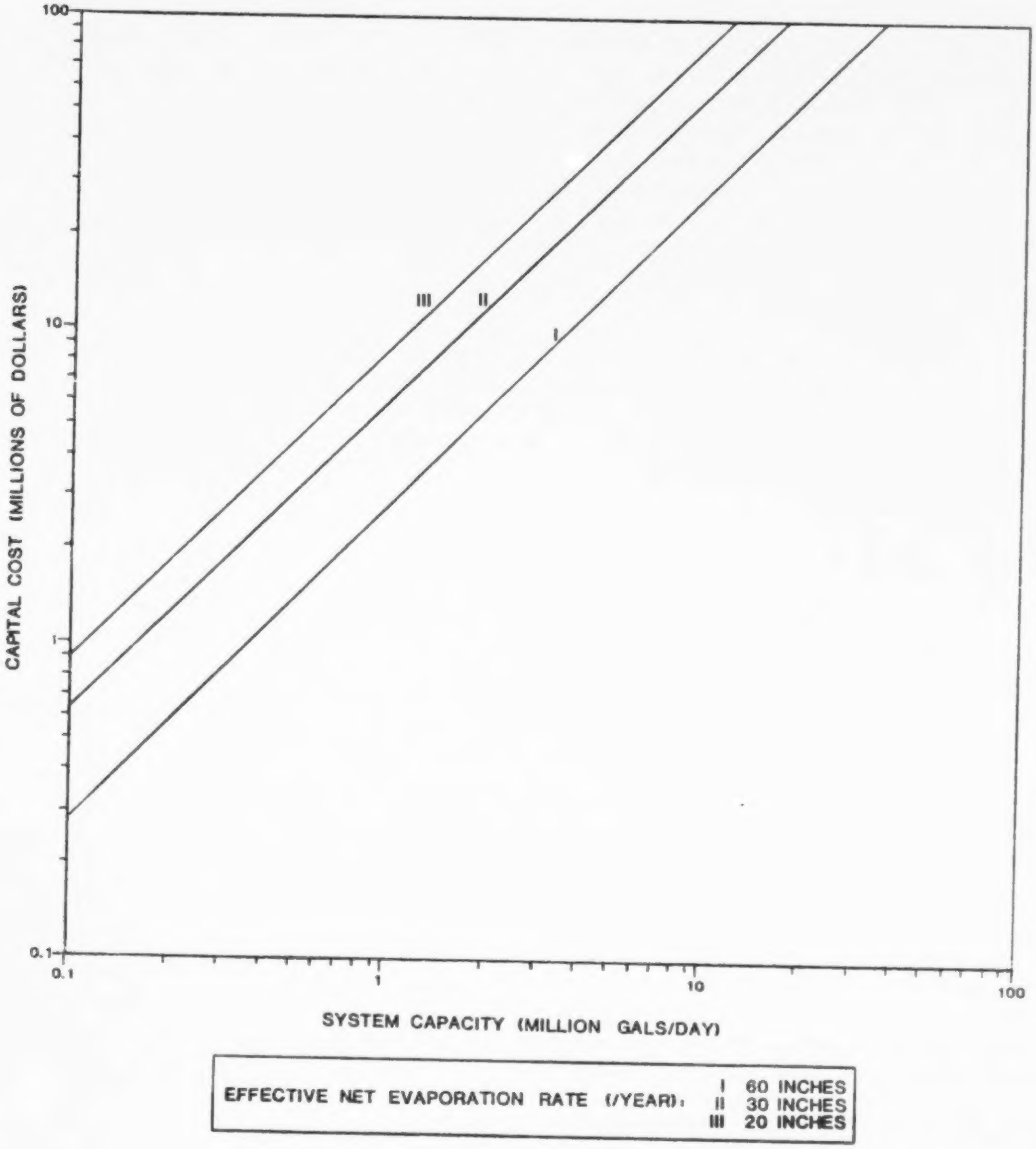

Figure 12. Capital costs for evaporation ponds.

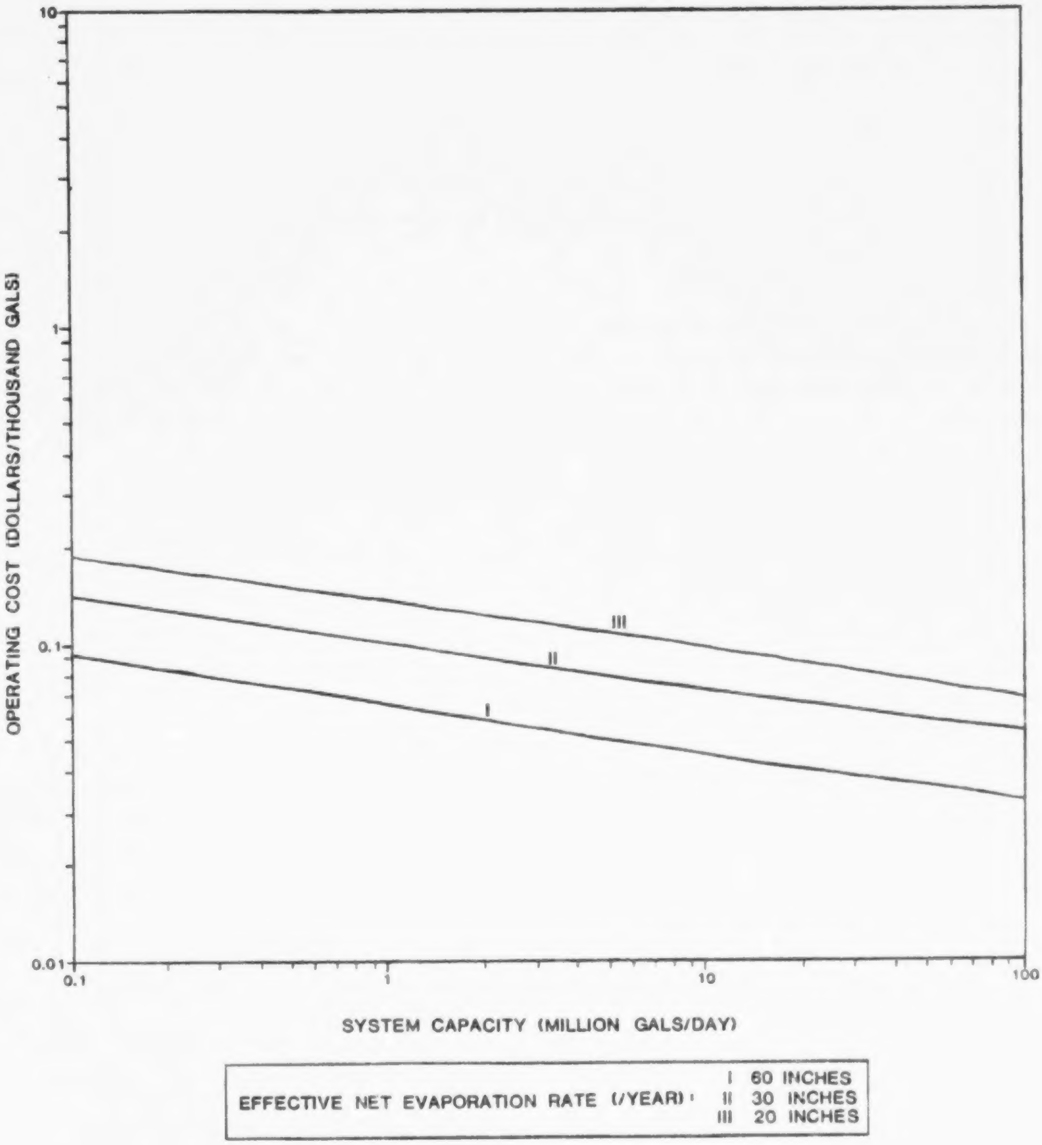

Figure 13. Evaporation pond operating costs.

Land Cost ($1,000/acre)	$ 100,000
Excavation and building dikes	$ 45,000
3-inch thick asphalt liner	$1,060,000
Pumps and lines (installed)	$ 10,000
TOTAL INSTALLED COSTS	$1,215,000

The 3-inch thick asphalt liner costs approximately $0.25/ft^2 (FO-130). If the land is not easily excavated, the cost will significantly increase. The operating costs are estimated to be $0.25/1000 gallons treated assuming that the solids can be allowed to accumulate on the bottom of the pond.

Secondary Emissions

For ponds designed to contain the precipitated solids, the only potential secondary emission would be pond seepage. Proper choice and installation of a liner should help eliminate or significantly reduce this potential. For ponds which are periodically dredged, the settled and precipitated solids removed would be a secondary emission requiring proper disposal.

OTHER TREATMENT TECHNOLOGIES

There are treatment technologies available other than the ones described previously which can also treat acid wastewaters for metal removal. These include activated carbon, ferrite coprecipitation, starch complexing, and sodium borohydride reduction. However, because of limited information and applicability, only a brief discussion of each is presented.

Activated Carbon

Activated carbon adsorption has long been a widely accepted method for the removal of organic contaminants from water and wastewater. The overall flexibility of the carbon adsorption process has resulted in its application in a wide variety of situations from oil refining to municipal wastewater treatment. Recently the use of carbon adsorption for trace metals removal has received more attention.

For organics the principal removal mechanism is physical adsorption onto the activated carbon. For heavy metals, however, adsorption is only one of several mechanisms which are thought to contribute to the system's removal abilities. Other possible mechanisms include precipitation, ion exchange, filtration or entrapment, and either reduction to metal or oxidation to insoluble forms. In some instances specially modified carbons, which take advantage of these other mechanisms, have been investigated with some success.

In true physical adsorption, the dissolved adsorbate (organic or metal) is attracted to the interior surface of the carbon where a dynamic equilibrium is established between a concentrated surface layer and the more dilute solution. Surface adsorption is usually not very uniform. Those surface sites which have unsatisfied valence bonds or surface charges will be the most "active" and adsorption at these sites will be the strongest. Although all portions of the surface, amounting to as much as 1200 m^2/g (5.86×10^6 ft^2/lb), are potential adsorption sites, many sites may be excluded if they lie within pores that are too small to accommodate extremely large adsorbate molecules (SM-190). Even so, true adsorption will occur most efficiently for large molecules (until the point that the molecule becomes too large with respect to pore size) with a minimum of surface charges and low solubility (SM-190).

Activated carbon can also remove metal contaminants by precipitation. For example, if a contaminant of very low solubility is present, the addition of activated carbon may cause the solution to become supersaturated (SM-190). The carbon provides a site for nucleation and a precipitate forms on the surface until the supersaturation condition no longer exists. Precipitation does not preclude additional contaminant removal by adsorption, but precipitation may clog pores and consequently reduce potential adsorption capacity.

Activated carbon possesses little ability to remove metals by ion exchange. Activated carbon will contain some functional oxygen-containing groups such as phenols, carboxyls, ethers, peroxides, lactones, and hydroxyls. The amounts and surface distribution of these groups will depend on the history of the adsorbent. In addition to the oxygen-containing groups, other groups containing sulfur and nitrogen may also be present. Typically these groups are cation acceptors and various metal cations will displace each other in a fashion consistent with ion exchange resins. For the most part, these randomly dispersed functional groups are fast acting and capable of removing the simple metal ions in the 1, 2, or 3+ valence states (SM-190).

Depending on the initial method of preparation, activated carbon will contain a variety of impurities which cause the carbon surface to act as an active catalyst for both reduction and oxidation. If the carbon has surface impurities of elemental iron, ferrous salts, and ferrous sulfides, then metal ions such as gold, silver, and mercury may be reduced to their elemental form. Similarly, a ferrous iron will quickly oxidize in the presence of dissolved oxygen to a ferric ion, which readily precipitates as $Fe(OH)_3$ when the pH is greater than 4 (SM-190).

Typical granular carbon adsorption systems consist of carbon bed contact equipment, any necessary pretreatment facilities, and carbon regeneration equipment, if economically practical. Pretreatment equipment is needed if excessive quantities of suspended solids, oil, or grease are present. If not removed, these constituents may filter out on the carbon and increase the pressure drop. Commonly used pretreatments are chemical clarification, oil flotation, filtration, and removal.

Following pretreatment, the wastewater stream is contacted with the activated carbon beds. Several different bed configurations are in use, but the most common arrangements are fixed beds in series or parallel, moving beds, or expanded upflow beds. For fixed beds in series, the flow is downward through adsorbers connected in series. For fixed beds in parallel, the flow is also downward through a parallel train of beds. Operation of the individual trains is staggered, so that exhaustion of the beds occurs sequentially. In moving beds, wastewater flows upward through the bed while portions of exhausted carbon are removed from the bottom of the unit and fresh carbon is added at the top. This design is very useful for systems requiring large amounts of carbon and countercurrent efficiency. In upflow operations, packed beds are expanded approximately 10 percent of their normal volume by flow (RI-152). This expansion allows the passage of suspended solids without an excessive pressure drop. The beds may be operated in parallel or series.

Following exhaustion, granular carbon must either be properly disposed of or reactivated. Landfilling is a very common disposal practice. The exhausted carbon is removed from the adsorber, drained of all liquids, and then dumped into a pit. The major advantage is the absence of reactivation equipment and the costs associated with such equipment. The major disadvantages are the increased operating costs resulting from the continuous purchase of replacement carbon and the possible environmental hazard of contaminant leaching following disposal.

Reactivation of spent carbon can be done either on-site or off-site. On-site reactivation is usually considered economically advantageous if the regeneration requirements exceed two hundred pounds of carbon per day (CO-098). For carbon exhausted by adsorption of organics, reactivation can be accomplished by partial thermal oxidation of the carbon in either multiple-hearth furnaces or rotary kilns at temperatures of 816 to 982°C (1500 to 1800°F). Due to attrition, about 5 to 10 percent of the carbon sent to reactivation is lost. If the spent carbon contains mostly adsorbed metals, reactivation can also be readily accomplished by acid wash (SM-190). No data is available to document the possible loss of metals by volatilization during this step.

Treatment of wastewater streams by activated carbon for metals removal has received serious consideration only in the last decade. Metals removal is more likely to occur by any of the mechanisms previously described other than true adsorption. For this reason the efficiency of an activated carbon system designed for metals removal will depend heavily on the overall composition of the feed stream and, subsequently, will be very site-specific. Recent studies have attempted to qualitatively evaluate the potential for metals removal by activated carbon. The results of these studies indicate that at least five metals (antimony, arsenic, bismuth, hexavalent chromium, and tin) show a high removal potential, while another four metals (silver, mercury, cobalt, and zirconium) display a good removal potential. A few other metals (lead, nickel, titanium, vanadium, and iron) show some removal potential. Several other metals (copper, cadmium, zinc, beryllium, barium, selenium, molybdenum, manganese, and tungsten) possess little or unknown removal potential (SI-A-192). These qualitative ratings do not necessarily imply that carbon adsorption cannot be successfully employed under specific circumstances. For example, a mining company has developed a process for concentrating and purifying molybdenum based on the adsorption of molybdenum blue (SM-190).

Ferrite Coprecipitation

The removal of heavy metals from acidic wastewaters by ferrite coprecipitation was developed in Japan (OK-024). The process, which produces a marketable residual, was originally developed for preparing high quality magnetic materials for industrial use. However, with increasing concern about removing heavy metals from wastewater, the ferrite coprecipitation process is now being considered as a possible heavy metal control technology.

The objective of ferrite coprecipitation is to convert the soluble metal ions in solution to insoluble magnetic oxides or ferrites which can be removed either magnetically or through tertiary filtration. This objective is accomplished basically by the addition of a ferrous salt, neutralization, and oxidation.

In the process, the heavy metal bearing wastewater is mixed with a divalent ferrous salt, usually ferrous sulfate ($FeSO_4 \cdot 7H_2O$). This ferrous salt is widely available and results as a waste product during the production of steel or titanium dioxide. The divalent iron ion (Fe^{++}) will coexist with the nonferrous metal ion in solution. Alkali is added to neutralize the acidic solution and a dark green hydroxide is formed as shown by the reaction:

$$xM^{++} + Fe^{++}_{(3-x)} + 6(OH)^{-} \rightarrow M_xFe_{(3-x)}(OH)_6 \qquad (6\text{-}24)$$

$x = 1,\ 2,\ 3$

Oxidation with air may follow during which redissolution and complex formation occurs yielding a black ferrite as shown from the reaction:

$$M_xFe_{(3-x)}(OH)_6 + \tfrac{1}{2}O \rightarrow M_xFe_{(3-x)}O_4 + 3H_2O \qquad (6\text{-}25)$$

Precipitates produced from this process are ferromagnetic and have relatively large particle sizes. Consequently, they can be removed effectively from solution either magnetically or through filtration (OK-024).

The relatively stable sludges produced from the process can be safely disposed of by landfilling or, alternatively, can be reused as a ferrite-ferromagnetic material. Ferrite precipitates do not have a tendency to redissolve and, consequently, potential leaching of heavy metals, if placed in a landfill, is minimized.

Ferrite coprecipitation performance data have been reported from two installations currently in operation in Japan. One installation is a test facility which uses a batch process to treat approximatley 1 m^3/hr (4.5 gpm) of wastewater at a laboratory in Kawasaki. Performance data reported for this test facility are provided in Table 15.

TABLE 15. PERFORMANCE DATA FROM A FERRITE COPRECIPITATION TEST FACILITY (Concentration, mg/ℓ)

Metal	Influent	Effluent
Mercury	7.4	0.001
Cadmium	240	0.008
Copper	10	0.010
Zinc	18	0.016
Chromium	10	>0.010
Nickel	1,000	0.200
Manganese	12	0.007
Iron	600	0.06
Bismuth	240	0.100
Lead	475	0.010

Source: OK-024

It can be observed that greater than 99 percent removal was achieved for all metal concentrations reported.

Another installation uses the ferrite coprecipitation process to treat approximately 4.5 m^3/hr (20 gpm) of off-gas scrubber liquor from a municipal refuse incinerator in Osaka. Performance data from these facilities are reported in Table 16. These data also show that very high removal efficiencies are achieved and that very low residual levels for most metals are attainable (OK-024).

Laboratory research is also being conducted in the United States by Industrial Filter and a pump manufacturing company. They report that ferrite coprecipitation is an effective process for the removal of heavy metals but no performance data have yet been released.

The major problem associated with ferrite coprecipitation reported to date is that it is more labor intensive than the more commonly used precipitation processes.

TABLE 16. PERFORMANCE OF FERRITE COPRECIPITATION IN OSAKA UNIT (Concentration, mg/ℓ)

Metal	Influent	Effluent
Mercury	6	0.005
Arsenic	0.7	<0.01
Trivalent Chromium	25	0.01
Hexavalent Chromium	0.5	not detectable
Lead	480	0.05
Cadmium	15	<0.01
Iron	3,500	0.04
Zinc	650	0.5
Copper	23	0.08
Manganese	60	0.5

Source: OK-024

Starch Complexing

Heavy metals can be removed from contaminated wastewaters by forming complex ions with insoluble modified starches. Xanthated starch currently appears to be the most promising for application on a commercial scale but other modified non-xanthate starches are being tested.

Xanthates can be synthesized by reacting an epichlorohydrin cross linked starch with carbon disulfide (CS_2) in the presence of sodium hydroxide (NaOH). The insoluble starch xanthate will react with soluble heavy metals in the presence of cationic polymers to form a complex salt. Heavy metals are removed as the product sludge is separated from solution (WI-316).

Two methods have been prepared for applying this technology on a commercial scale. One method suggests mixing the starch xanthate and polymer with the contaminated influent in a reaction tank and pumping the solution to pressure filters where the complexed metals are separated. Sludge containing the complexed metals is removed by filter backwashing. Another method recommends precoating a tertiary filter with the starch xanthate. As the wastewater passes through the filter, the soluble heavy metals will form complex ions and precipitate in the modified filter (ZI-A-034).

Performance data for facilities using starch xanthate is relatively scarce. However, a pump manufacturing company has conducted laboratory studies in a pilot plant used to polish treated effluent from a metal finishing facility. Typical results reported from their investigation for removing copper, lead, and mercury are presented in Table 17.

TABLE 17. TYPICAL PERFORMANCE DATA USING STARCH XANTHATE

Metal	Concentration, mg/ℓ Influent	Concentration, mg/ℓ Effluent
Copper	31.7	0.020
Lead	10.3	0.025
Mercury	100.0	0.003

Source: ZI-037

It can be observed that very low effluent concentrations are attainable and that starch xanthate appears to be especially effective for removing of mercury.

The U.S. Department of Agriculture has also conducted studies on the use of starch xanthate at the Agricultural Research Service (FL-S-092). The results of their studies are shown in Table 18. These results were obtained by reacting the contaminated wastewater with the approximate stoichiometric quantities of reagent. These results also indicate that very high removal efficiencies are attainable.

TABLE 18. HEAVY METAL REMOVAL EFFICIENCIES USING STARCH XANTHATE AS DETERMINED BY USDA

Metal	Concentration, mg/ℓ Influent	Concentration, mg/ℓ Effluent
Copper	31.8	0.007
Nickel	29.4	0.019
Cadmium	56.2	0.009
Lead	103.6	0.025
Trivalent Chromium	26.0	0.003
Silver	53.9	0.245
Zinc	32.7	0.046
Iron	27.9	not detectable
Manganese	27.5	1.630
Mercury	100.0	0.004

Source: WI-309

Modified nonxanthate starches are also being investigated for possible use in heavy metal removal. These starches are reported to have approximately one-half the removal capacity of xanthated starches and cost approximately one-half as much. Consequently, approximately twice the sludge volume can be anticipated for equivalent removal efficiencies (ZI-034). This occurs because the unreacted nonxanthate starch precipitates along with the portion reacting with the metal ions.

Disposal of process residuals or sludges is a major problem associated with the starch xanthate process. Laboratory test results indicate that heavy metal removal capacity is approximately 0.0011 moles per gram of starch (ZI-034). Consequently, relatively large sludge volumes will be produced for the quantity of heavy metals removed. Conventional land disposal does not appear to be an environmentally acceptable alternative because the organic structure of the starch xanthate-metal sludge can decompose rapidly and release the metal to the environment. Incineration is being considered for possible metal recovery but off-gas scrubbing facilities would be necessary to insure that heavy metals are not emitted to the atmosphere. Additional costs associated with these stack gas control facilities may be prohibitive. Also, the heavy metals collected in the scrubber liquor would again have to be removed before the liquor could be reused or discharged to a receiving stream.

Several possibilities for recovering heavy metals for their commercial value have also been investigated. The starch xanthate-metal complex can be broken with either acid or heat treatment. However, the development of this technology is still in the initial stages and little information is available for an adequate assessment. Charging the process residuals to a smelter furnace for enhanced metal recovery has also been considered, but economics will be difficult to justify because of the relatively large ratio of sludge volume to metal contents.

The application of the starch xanthate process is most promising if considered as a polishing technology following a more conventional process rather than a substitute treatment alternative. Sludge quantities can be considerably reduced thereby minimizing the ultimate disposal problem. However, other associated problems must also be considered. Starch xanthates lose their removal effectiveness when cyanides are present. Consequently, the process is severely limited if cyanides are not previously removed. Additionally, insoluble starch xanthates lose their complexing capacity rather rapidly and on-site manufacturing is recommended. Caution must be taken when handling the poisonous carbon disulfide used to synthesize the xanthates at the treatment facility.

Sodium Borohydride

Sodium borohydride ($NaBH_4$) is a mild but highly effective reducing agent. In practice this water soluble reagent can be added to contaminated wastewaters to reduce heavy metal ions to their neutral state for removal and/or recovery by filtration.

Aqueous borohydride reductions of metals in solution generally proceed by the intermediate formation of a metal hydride or borohydride which is unstable in water and decomposes to produce the free metal. The basic treatment processes for sodium borohydride reduction are similar to chemical precipitation. Treatment includes pH adjustment, sodium borohydride addition for reduction and precipitation, and clarification and/or filtration for solids-liquids separation. The treated effluent may require additional polishing which can be accomplished with a carbonaceous absorbent or suitable chelate or exchange resin (JU-A-043). The sludge that is produced consists mainly of elemental metals and expensive sludge handling facilities and ultimate disposal problems can possibly be avoided. However, if multimetal ions are present and recovery is desirable, metals separation will be necessary.

The reducing strength of sodium borohydride is greatest under strongly basic conditions but the kinetic rate of reduction is accelerated as the pH decreases. This phenomenon suggests that an optimum pH for a specific reaction exists. Basic solutions of sodium borohydride are generally quite stable and pH conditions below 8.0 are conducive to borohydride decomposition resulting in excessive consumption of borohydride and liberation of an explosive hydrogen gas as shown from the reaction:

$$BH_4^- + 4H_2O \rightleftarrows B(OH)_4^- + 4H\uparrow \qquad (6\text{-}26)$$

At high pH conditions the rate of reduction decreases the process efficiency. Consequently, a pH range of 8.5 to 9.0 is generally desirable and additional safety precautions, including adequate ventilation and elimination of potential ignition sources should be maintained (ZI-A-034, VE-073).

Sodium borohydride is relatively expensive, costing approximately $15 per pound, and should only be used with highly efficient mass transfer or mixing facilities to insure optimization of the borohydride-metal reactions. Applications should be limited to wastewaters containing small or trace levels of metallic ions. Additionally, sodium borohydride should only be considered for use in either batch processes or in continuous processes where a constant influent metal content is maintained (ZI-A-034).

In batch processes, the calculated quantity of sodium borohydride is generally added in small portions after neutralization. An excess of borohydride is usually desirable not only to insure rapid and complete reduction but also to maintain a strong reducing environment preventing re-dissolution of the metal by dissolved oxygen or complex formation. A reaction time of at least five minutes is usually necessary (JU-A-043).

Sodium borohydride is currently being used on a commercial scale to recover silver from photographic fixing solutions by reducing the silver-thiosulfate complex to elemental silver. Although the cost of the reagent is relatively high, process operating costs are somewhat minimized owing to the stoichiometric ratios of 1 to 8 as shown from the reaction:

$$8Ag^+ + BH_4^- + 2H_2O \rightleftarrows 8Ag\downarrow + BO_2^- + 8H^+ \qquad (6\text{-}28)$$

From this reaction it can be calculated that one pound of borohydride ion will remove 22 pounds of silver (VE-073).

Sodium borohydride is also being used successfully to recover mercury compounds from wastewaters emanating from chlor/alkali plants. The soluble inorganic mercury compounds are reduced at a pH of 9.0 and are removed by filtration. In this application, one pound of sodium borohydride can theoretically remove in excess of 21 pounds of mercury based on the following reaction:

$$4Hg^{++} + BH_4^- + 8OH^- \rightleftarrows 4Hg\downarrow + B(OH)_4^- + 4H_2O \qquad (6\text{-}28)$$

Mercury which appears in the organic form must first be released through oxidation before borohydride treatment will be effective (VE-073).

Sodium borohydride is also effective for the removal and recovery of dissolved lead compounds, including lead salts from wastewaters generated from the manufacture of tetra-alkyl lead compounds. In this application, both inorganic and organic lead is reduced to the elemental form in one step (VE-073).

Little performance data for actual sodium borohydride treatment facilities have been reported and dosage rates and anticipated removal efficiencies are not presented. However, a mercury level as low as 0.01 mg/ℓ has been reported for wastewater treatment at chlor-alkali plants. In general, sodium borohydride is reported to be effective for the removal and/or recovery of cadmium, mercury, lead, silver, and gold (VE-073). Capital costs of $667/1,000 gallons per day and operating costs between 6.7 and 26.7 cents per 1,000 gallons have been reported (PA-322).

SECTION 7

SOURCES OF EFFLUENTS CONTAINING METAL IN THE NONFERROUS METALS INDUSTRY

INTRODUCTION

This section identifies the sources of acidic wastewater in the primary and secondary copper, lead, and zinc segments of the nonferrous metals industry. For the primary industry, wastewater sources can be divided into the following four categories:

- Mining
- Concentrating
- Smelting
- Refining

The mining and concentrating categories account for the largest quantity of wastewater at any particular smelting facility (69 to 90 percent) but the concentration of any particular metal ion is relatively low (typically <1 mg/ℓ). Smelter and refinery wastewaters, however, are relatively low volume and may have metal ion concentrations ranging from <1 to 1000 mg/ℓ.

Smelter/refinery wastewater can be further classified into contact and non-contact water. Gas scrubbing water and washwater are typical contact wastewaters. These contain high concentrations of metal ions (1 to 1000 mg/ℓ). Mold cooling water or water jacket cooling water are typical noncontact wastewaters and normally contain less than 1 mg/ℓ of any particular contaminant.

For the secondary industry, wastewater sources can be divided into the following three categories:

- Scrap pretreatment
- Smelting
- Refining

The wastewaters from these categories are sometimes difficult to identify separately because of the close proximity of each type of process within a particular smelter. In addition, washwater and leaks or spills are likely to contribute a larger percentage of the total effluent than in the primary metals industry. As in the primary smelting/refining category, wastewater can be classified as either contact or non-contact with the same relative difference in metal ion concentrations.

In this section, brief industry descriptions are presented for each primary and secondary industry. The sources of wastewater in each industry are then identified and the data available on each wastewater are summarized. No attempt has been made to separate wastewater generated by washdowns or general housekeeping from the process wastewater reported in the literature.

PRIMARY COPPER INDUSTRY

Industry Description - Primary Copper

Copper is produced primarily from sulfide ores which typically contain 0.6 to 1.5 percent copper. Raw ore is concentrated in a series of crushing, grinding, classifying, and flotation steps to produce a concentrate which normally contains 15 to 30 percent copper. This concentrate may be prepared for smelting by drying or roasting or it may be charged directly to a smelting furnace.

Mining of low grade porphyry (fine-grained, dark red or purplish igneous rock) copper is done primarily in large open pit mines. Drilling, blasting, loading, and hauling operations take place before the ore is transported to the beneficiation processes. In general, mining operations account for approximately 25 percent of the cost of copper manufacture.

Ore bodies normally lie under an overburden of country rock. The overburden may be dumped as waste, used for road construction, or leached to extract the very low grade of copper (0.1 to 0.4 percent) it contains. Leaching involves the slow oxidation of copper sulfide salts in the presence of water followed by precipitation on iron scrap. The precipitated copper is dewatered and recovered as a slurry or pulp that is referred to as cement copper. Cement copper ranges from 70 to 90 percent copper and can be used as a smelter feed. Not all mines leach their waste rock.

The concentration phase of copper production is necessary because of the low copper content of a typical ore (0.6 to 1.5 percent copper). Production of 300 tons per day of blister copper from a moderate size smelter involves concentrating over 4200 tons of ore per day. Crushing, grinding, classifying, and ore flotation steps are used to obtain a concentrate containing 15 to 30 percent copper. Roughly 97 percent of the ore is normally discarded as waste rock in tailings ponds near the concentrator site. The concentrate is filtered and thickened before being sent to the smelter.

There are 16 primary copper smelters operating in the United States at present. Twelve of these smelters are operated by companies which produce their own smelters which purchase and blend concentrates prior to processing them at the smelter. There are eleven copper refineries operating in the United States at present.

Wastewater Source Identification - Primary Copper

Mining, concentration, smelting, and refining of copper in the United States are accomplished in steps which have become standard in the past 50 to 70 years. Table 19 lists each of the processes for which effluent streams have been identified and summarizes the available data on the characteristics of these process specific wastewaters. The following discussion describes the sources of these wastewaters in more detail.

Mining--

Mining methods are determined by the size, depth, and configuration of the ore body. Both open-pit and underground copper mines are currently operating in the United States. Wastewater from copper mining comes from seepage or runoff from the mine or spoil dumps, and from the water sent into the mine for utility uses. The wastewater from open-pit copper mines ranges from zero to 0.3 cubic meter of water per metric ton of ore mined. From underground mines, the amount ranges from 0.008 to 4.0 cubic meter per metric ton of ore. Chemical characteristics are typical of those from any sulfide mine, as given in Table 20.

Spoil is waste rock moved during the mining process as overburden, in the construction of shafts and tunnels, or as low grade inclusions found within the ore body. It is disposed of near the mine workings. The spoil generally contains appreciable amounts of sulfide minerals. These spoils are placed where they are also exposed to rainfall, seepage, and surface runoff.

In mining the main body of the ore, stockpiles of ores are frequently placed either near the mine or near the mill, or both, in order to avoid having to synchronize operations of these two processes. The stockpiles are also exposed to the weather, and in some cases are purposely hosed down to minimize blowing dust.

All of the large open-pit mines are in regions of deficient rainfall, and some are in desert areas. Natural evaporation within the pit greatly reduces the volume of wastes that must be pumped out, and seepage from spoil dumps rarely enters a stream. The water that accumulates is in many cases disposed of merely by pumping it onto a nearby flat area, where it either seeps into the alkaline soil or evaporates.

Ore Concentrating--

Concentrating consists of crushing and grinding the ore to a fine powder, and then separating the minerals by froth flotation. In milling, the ore is sent through crushers and then through fine grinders. Between each stage, it is classified (screened), and the final milled product is a mixture of particles between 65 and 200 mesh.

Flotation is the step where the copper-containing particles are actually separated from the gangue or country rock. In this process, the finely ground ore is introduced into a series of flotation cells which are sparged

TABLE 19. SUMMARY OF POLLUTANTS IN INDUSTRIAL WASTEWATER SOURCES - PRIMARY COPPER

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)			Ref.	Comments
Primary Copper Industry						
Mining						
- Mine wastewater			Underground	Open-Pit	PE-274	Major potential source of water pollution from this industry. Impact somewhat lessened by location of most mines in arid regions.
• underground mine	3815 m^3/day	pH	7.37	6.96		
• open-pit mine	409 m^3/day	Cu	0.87	1.05		
		Se	<0.077	0.096		
		As	<0.07	<0.01		
		Zn	2.8	0.1		
		Sb	<0.5	<0.5		
		Fe	<0.1	<0.1		
		Mn	2.22	0.9		
		Cd	<0.02	<0.03		
		Ni	<0.05	<0.05		
		Mo	<0.5	<0.2		
		Hg	<0.0001	<0.0001		
		Pb	<0.1	<0.5		
Concentrating						
Ore flotation water	100-500 m^3/m ton concentrate	As	~0.07		PE-274	Largest source of wastewater in the industry. Used to sluice tailings to pond. Partial reuse of pond water.
		Sb	0.2 -1.0			
		Cd	0.02 -0.05			
		Cu	0.08 -very high			
		Co	0.04 -1.68			
		Fe	0.1 -2.0			
		Mn	0.05 -4.8			
		Hg	0.001-0.05			
		Mo	0.2 -20			
		Ni	0.05 -3			
		Pb	0.01 -3			
		Ag	~0.1			
		Se	0.003-0.02			
		Zn	0.05 -8.50			
		CN^-	0.01 -0.1			

NOTE: P = present, but levels not quantified.

(Continued)

TABLE 19 (Continued)

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)				Ref.	Comments
Primary Copper Industry (Cont'd)							
Slag Flotation						PE-274	
- Run-off from slag granulation			Plant 103	Plant 110	Plant 120		Quantity and composition is highly variable.
		pH	7.7	8.1	6.4-7.6		
		CN^-	0.005	0.050	0.030		
		As	3.7	0.048	5.70		
		Cd	0.001	0.001	0.042		
		Cu	0.12	0.05	0.604		
		Fe	0.04	0.03	340		
		Pb	0.04	0.070	7.4		
		Hg	0.0001	0.0001	0.0001		
		Ni	0.001	0.06	0.16		
		Se	0.001	0.54	0.040		
		Zn	0.44	0.023	36		
Contact Sulfuric Acid Plant							
Off-gas scrubber liquor (i.e., acid plant blowdown)	.147-10.1x 10^6 ℓ/day			Range for 3 Plants (kg/m. ton)		PE-274	Essentially a weak H_2SO_4 solution that cannot be marketed. This stream frequently combined with other plant effluents for treatment or recycle.
		pH		1.8 -2.5 pH units			
		CN^-		0 -0.0024			
		As		0.004 -0.129			
		Cd		0.0002-0.0276			
		Cu		0.0001-[188.2]			
		Fe		0.0014-0.1116			
		Pb		0.0051-0.2501			
		Hg		0 -0.0002			
		Ni		0 -0.0030			
		Se		0 -0.0268			
		Zn		0.0017-0.436			

NOTE: P = present, but levels not quantified.

(Continued)

TABLE 19 (Continued)

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)	Ref.	Comments
Primary Copper Industry (Cont'd)				
DMA SO_2 Sorption				
- Off-gas scrubber liquor		Similar to Contact Sulfuric Acid Plant	PE-274	
- Purge stream from DMA unit	18 kg/m ton SO_2 prod.	Typical composition: 4.5 percent TDS 25 mg/ℓ DMA 18 mg/ℓ suspended solids pH 5.8	PE-274	
Arsenic Recovery				
- Arsenic plant wash-down water		As 310.0 Cu 88.4 Zn 37.0 Pb 7.7 Cd 1.05 Hg 0.0003 Se 0.04 Ni 0.75 Fe 9.4 CN^- 0.01 pH 3.8-4.4	PE-274	Plant is washed down on a daily basis. Water is mixed with another waste and discharged to a pond.
Anode Refining and Anode Casting				
- Anode cooling water	950,000 ℓ/day	Net Change, mg/ℓ* Cl^- 8.7 Al 0.12 As 0.01 Cu 8.53 Zn 0.25		*Water used for cooling is generally a recycle stream from some other process step.

NOTE: P = present, but levels not quantified.

(Continued)

TABLE 19 (Continued)

<table>
<tr><th>Source</th><th>Flow (ℓ/min)</th><th colspan="2">Stream Composition (mg/ℓ)</th><th>Ref.</th><th>Comments</th></tr>
<tr><td colspan="6">Primary Copper Industry (Cont'd)</td></tr>
<tr><td colspan="6">Electrolytic Refining</td></tr>
<tr><td>- Spent H_2SO_4 electrolyte</td><td></td><td>Cu
As
Sb
Bi
Ni</td><td>45,000-50,000
500-12,000
200-700
100-500
2,000-20,000</td><td>PE-274
EN-392</td><td>Some refineries reclaim the Cu values from this stream; however, in other cases this stream constitutes a significant waste effluent.</td></tr>
<tr><td colspan="6">Electrolyte Purification</td></tr>
<tr><td>- Electrolyte acid purge or "black acid"</td><td></td><td>As
Sb
Bi</td><td>P
P
P</td><td>PE-274</td><td></td></tr>
<tr><td>- Evaporated water from the electrolyte</td><td></td><td></td><td></td><td>PE-274</td><td>Usually mixed with steam condensate and direct cooling water in barometric leg discharge devices.</td></tr>
<tr><td colspan="6">Melting and Casting Cathode Copper</td></tr>
<tr><td>- Cooling water for cast shapes</td><td>320,000 ℓ/day in one case</td><td colspan="2">
<table>
<tr><th></th><th colspan="3">Plant X</th><th colspan="2">Plant Y</th></tr>
<tr><th>Parameter</th><th>Inlet water</th><th>Wirebar cooling</th><th>Semicontinuous cake casting</th><th>Inlet water</th><th>Wirebar cooling recycle</th></tr>
<tr><td>pH</td><td>7.6</td><td>7-8</td><td>8.0</td><td>7.1-7.6</td><td>8.0-8.4</td></tr>
<tr><td>As</td><td>0.001</td><td>0.001</td><td>0.001</td><td>0.001</td><td>0.001</td></tr>
<tr><td>Cd</td><td>0.001</td><td>0.001</td><td>0.001</td><td>0.0008</td><td>0.0021</td></tr>
<tr><td>Cu</td><td>0.30</td><td>0.69</td><td>0.18</td><td>0.021</td><td>3.5</td></tr>
<tr><td>Fe</td><td>0.02</td><td>0.13</td><td>0.04</td><td>1.2</td><td>1.7</td></tr>
<tr><td>Pb</td><td>0.007</td><td>0.007</td><td>0.003</td><td>0.078</td><td>0.068</td></tr>
<tr><td>Hg</td><td>0.00350</td><td>0.00425</td><td>0.0001</td><td>0.00004</td><td>0.00004</td></tr>
<tr><td>Se</td><td>0.001</td><td>0.001</td><td>0.001</td><td>0.040</td><td>0.040</td></tr>
<tr><td>Zn</td><td>0.001</td><td>0.067</td><td>0.001</td><td>0.35</td><td>0.88</td></tr>
</table>
</td><td></td><td></td></tr>
</table>

NOTE: P = present, but levels not quantified.

(Continued)

TABLE 19 (Continued)

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)	Ref.	Comments
Primary Copper Industry (Cont'd)				
Doré Metal Separation				
- Electrolyte acids	Few gallons intermittently		PE-274	This represents a relatively insignificant waste stream.
Heap and Vat Leaching				
- Spent leaching stream	350,000-1,000,000 ℓ/m ton Cu produced	Fe very high	PE-274	
Solvent Extraction				
- Bleed stream from concentrated acid used to complex Cu from extractant		Fe P As P Zn P	PE-274	
Electrowinning				
- Water from cathode cleaning			PE-274	
Arbiter Precipitation				
- Filtrate from precipitation		Ammonium sulfate solution containing unprecipitated Cu.	PE-274	
- Filter backwash			PE-274	Slurry
Arbiter Decomposition				
- Filtrate		Ammonium sulfate solution.	PE-274	Similar to stream from Arbiter precipitation but containing less Cu.

NOTE: P = present, but levels not quantified.

TABLE 20. RAW WASTE LOAD IN WATER PUMPED FROM SELECTED COPPER MINES

Parameter	Underground Mine		Open-pit Mine	
	Concentration (mg/ℓ)	Raw waste load per unit ore mined (kg/1000 metric tons)	Concentration (mg/ℓ)	Raw waste load per unit ore mined (kg/1000 metric tons)
Flow	3,815.3 m^3/day	17.28 m^3/1000 metric tons	409 m^3/day	75 m^3/1000 metric tons
pH	7.37[a]	7.37[a]	6.96[a]	6.96[a]
TDS	29,250.0	5,053.9	1,350.0	101.0
TSS	69.0	11.9	2.0	0.2
Oil & Grease	<1.0	<0.173	7.0	0.5
TOC	<4.5	<0.778	10.0	0.75
COD	819.0	141.5	4.0	0.3
B	2.19	0.378	0.07	0.005
Cu	0.87	0.150	1.05	0.08
Co	<0.04	<0.007	<0.06	<0.005
Se	<0.077	<0.013	0.096	0.007
Te	0.60	0.104	<0.2	<0.02
As	<0.07	<0.012	<0.01	<0.0008
Zn	2.8	0.484	0.1	0.008
Sb	<0.5	<0.086	<0.5	<0.04
Fe	<0.1	<0.017	<0.1	<0.008
Mn	2.22	0.384	0.9	0.07
Cd	<0.02	<0.003	<0.03	<0.002
Ni	<0.05	<0.009	<0.05	<0.004
Mo	<0.5	<0.086	<0.2	<0.02
Sr	119.0	20.6	0.8	0.06
Hg	<0.0001	<0.00002	<0.0001	<0.000008
Pb	<0.1	<0.017	<0.5	<0.04

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[a] Value in pH units.

with air after flotation agents are introduced. Flotation agents such as pine oil or long chain alcohols are used to generate froth. Chemicals known as "collectors" are also added which preferentially adsorb on the ore particle surfaces. This changes the properties of the ore particles so that they attract bubbles preferentially over the gangue particles (or vice versa). The ore concentrates in the interstitial liquid in the froth bubbles while the gangue sinks and passes out of the cell as tailings.

This process is the largest source of wastewater in the industry. The ore flotation water is used to sluice the tailings into a pond. Although part of the water is recycled to the plant, the remainder is discarded. The volume of wastewater from this process plus the amount lost by evaporation will equal the water consumption, ranging from 100 to 500 cubic meters per metric ton of concentrate. A continuous bleed of this milling and flotation water is necessary. Reported analyses indicate that the water from the concentrator may contain up to 3500 mg/ℓ of dissolved solids, from 0.01 to 0.01 mg/ℓ of cyanides, and the following ranges of metallic elements (PE-274):

Element	Concentration, mg/ℓ
Arsenic	0.07 approximately
Antimony	0.2 to 1.0
Cadmium	0.02 to 0.05
Copper	0.08 to very high
Cobalt	0.04 to 1.68
Iron	0.1 to 2.0
Manganese	0.05 to 4.8
Mercury	0.001 to 0.05
Molybdenum	0.2 to 20
Nickel	0.05 to 3
Lead	0.01 to 3
Selenium	0.003 to 0.02
Silver	0.1 approximately
Strontium	0.03 to 2.5
Zinc	0.05 to 8.50

The water may also contain thiosulfates and thionates, and the materials, both inorganic and organic, used as flotation additives.

Slag Flotation--

This process is similar to the ore concentration process. The feed stream, however, is slag produced from either a smelting or converting furnace rather than raw ore. The operating principle is the same in that sulfide materials are recovered in the flotation froth and the waste material sinks and is discarded as tailings.

Slag produced in electric, flash, or continuous smelting furnaces or in copper converters contains too much copper to be discarded. Consequently, the slag must be treated either in a cleaning furnace or in a flotation mill. The tapped slag is slow cooled, crushed, and sent to a concentrator. Flotation produces a high copper content concentrate which is recycled to the smelting furnace feed preparation area. An iron-rich tailings (0.5 weight percent Cu) is discharged.

Water used for cooling and flotation is recycled until impurities build up which reduce the flotation process efficiency. A bleed stream is then removed and typically discharged to the ore concentration tailings pile. No data is available on the characteristics of this effluent stream.

Contact Sulfuric Acid Plant--

For the most part, sulfuric acid is currently produced by the Contact Process. In the Contact Process, sulfur dioxide is reacted with oxygen over a vanadium pentoxide catalyst to form sulfur trioxide. The sulfur trioxide then combines with water in an absorber where the product acid is formed. Older contact acid plants operated at 95 to 97 percent sulfur dioxide conversion efficiencies (WA-219). At these efficiencies, significant quantities of sulfur dioxide were emitted to the atmosphere. This problem has been overcome by modifying the Contact Process to create a Double Catalysis/Double Absorption (DC/DA) Process. According to Browder (BR-283), if a DC/DA Process is used to produce sulfuric acid, sulfur dioxide to acid conversion efficiencies ranging from 99.7 to 99.9 percent can be achieved. Thirteen of the copper smelters in this country operate contact sulfuric acid plants to treat all or part of the gases from the metallurgical operations.

A typical flow diagram of the Browder DC/DA Process is illustrated in Figure 14. The feed gas to the process typically consists of 8.4 to 9.0 volume percent SO_2 and 8.6 to 9.2 volume percent O_2 on a dry basis. Some conditioning of the feed gas is usually performed prior to its entry into the acid plant. Gas conditioning is normally accomplished in a series of two or three towers.

- A hollow tower with water spray for gas cooling and dust removal.
- A packed tower with water spray for final temperature, humidity, and dust control.
- A mist eliminator to precipitate entrained droplets.

The gas conditioning towers (which are not illustrated in Figure 14) act as a buffer to changing gas stream conditions (water content, dust loading, temperature, oxygen content). The blowdown from these towers is one potential source of wastewater from a sulfuric acid plant.

The hollow tower cools the inlet gas to approximately 58°C (137°F) with a water spray. Some particulate matter is scrubbed by the water spray, but gas cooling is the major function of the tower.

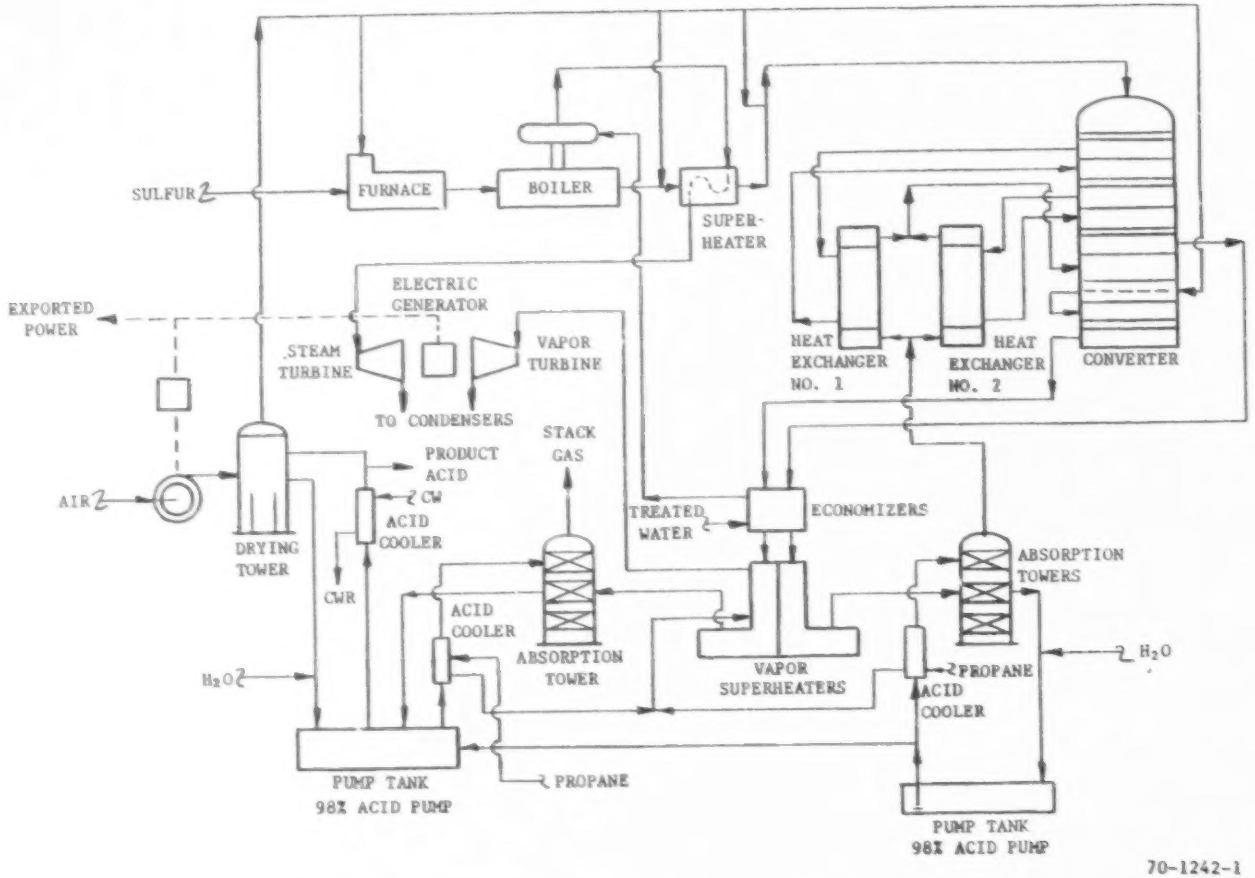
SULFUR
FURNACE
BOILER
SUPER-HEATER
ELECTRIC GENERATOR
EXPORTED POWER
STEAM TURBINE
VAPOR TURBINE
TO CONDENSERS
AIR
DRYING TOWER
PRODUCT ACID
CW
ACID COOLER
CWR
H₂O
PUMP TANK 98% ACID PUMP
ACID COOLER
ABSORPTION TOWER
STACK GAS
PROPANE
TREATED WATER
ECONOMIZERS
VAPOR SUPERHEATERS
ABSORPTION TOWERS
PROPANE
ACID COOLER
H₂O
PUMP TANK 98% ACID PUMP
HEAT EXCHANGER NO. 1
HEAT EXCHANGER NO. 2
CONVERTER
70-1242-1

Figure 14. Typical flow diagram of Browder DC/DA process for a metallurgical plant.

Source: PA-205

The packed tower controls gas temperatures to meet the water balance for the acid plant. Combustion gases containing large amounts of water may require refrigeration to remove enough water to allow strong acid to be produced. Typical gas outlet temperature is 40°C (104°F) from this tower at -10 to -14 inches H_2O pressure.

Humidified gas from the packed tower passes through a mist eliminator to remove any sulfuric acid mist present in the gas. Acid mist may form from SO_3 present in the gas reacting with water sprays upstream of the mist eliminator. Mist eliminators can be lead-piped electrostatic precipitators or simply a corrosion-resistant packing which removes the mist from the gas stream. Following the gas-conditioning section, air is added to the gas stream if insufficient oxygen is present for the catalytic reaction.

These gas conditioning columns create off-grade weak acid that cannot be sold. The amount is estimated as 4 to 8 liters for each 10 cubic meters of gas treated. Table 21 provides typical analyses for this acid plant blowdown. Acid plant blowdown is sometimes mixed with other waters for treatment or recycle. Table 22 lists the practices of the existing smelter acid plants. If large volumes of strong acid must be neutralized, the only tested, economical method of disposal is treatment with limestone, followed by more precise pH adjustment with lime.

After passing through the gas conditioning towers, the feed gas enters a drying tower. The dry gas then passes through a series of heat exchangers to bring the gas temperature to 435°C (815°F). This hot gas then passes through three catalyst beds with intermediate heat exchange.

After the third catalyst bed, the gas is fed to an absorber where the SO_3 is absorbed in a circulating acid stream. The vapor is sent to a fourth catalyst bed. The outlet gas from the last bed is routed to a second absorption tower where the remainder of the SO_3 is absorbed by circulating acid. After the second absorption tower, the gas passes through a demister to remove any entrained acid mist before being vented through a stack.

Sulfuric acid from the absorption towers flows to an acid pump tank where it is diluted, if necessary, to maintain the required strength for absorption. The acid is then pumped through a series of coolers before it is returned to the absorption towers. A stripping tower is used to remove dissolved sulfur dioxide from the acid fed to the final absorption tower. Product acid is removed from the second stage absorption system through product coolers before it is sent to storage.

DMA SO_2 Absorption--

The DMA Absorption process scrubs SO_2 from a gas stream, then releases the SO_2 as a concentrated stream. Waste gases are first cleaned of particulate matter and dried as described previously in this Section under Contact Sulfuric Acid Plant. Next, most of the SO_2 is absorbed by dimethylaniline (DMA) as the gases pass through a scrubber. The gases are then scrubbed with sodium carbonate to remove the remaining SO_2, then with weak sulfuric acid to reclaim the DMA in the gas stream. These three steps take place in a single

TABLE 21. RAW WASTE CHARACTERIZATION: ACID PLANT BLOWDOWN

Parameter	Units	Plant 1	Plant 2	Plant 3	Average
pH	pH	2.0-2.5	1.8	2.0	2.0
TDS	kg/metric ton		78.5	410.0	244.0
TSS	kg/metric ton		0.102	3.74	1.92
$SO_4^=$	kg/metric ton	[0.99][a]	7.69	64.0	36.0
CN^-	g/metric	0.0000	0.0000	0.0024	0.0008
As	kg/metric ton	0.044	0.129	0.004	0.059
Cd	kg/metric ton	0.0002	0.0014	0.0276	0.0097
Cu	kg/metric ton	0.0001	0.0018	[188.2]	0.0010
Fe	kg/metric ton	0.0014	0.0015	0.1116	0.0382
Pb	kg/metric ton	0.0051	0.0142	0.2501	0.0898
Hg	kg/metric ton	0.0000	0.0000	0.0002	0.0001
Ni	kg/metric ton	0.0000	0.0000	0.0030	0.0010
Se	kg/metric ton	0.0001	0.0000	0.0268	0.0090
Te	kg/metric ton	0.0000	0.0000	--	0.0000
Zn	kg/metric ton	0.0017	0.215	0.436	0.218
Oil & Grease	kg/metric ton	0.0000	--	0.0	0.0
Flow, 10^6	ℓ/day	0.147	4.16	10.1	--
Production	metric ton/day	311.(62)	528.(264)	655.(393)	--
Flow/Prod	kg/metric ton	2,400.0	15,800.0	25,700.0	14,700.0

---

[a] Bracketed values not used in averaging computation.

TABLE 22. ACID PLANT BLOWDOWN CONTROL AND TREATMENT PRACTICES

Plant	Discharge	Control and/or treatment practice
1	0	Blowdown neutralized with ammonia and used to precondition converter gases prior to hot ESP. No discharge.
2	0	2/3 of blowdown to reverb brick flue spray chamber for cooling reverb gases, other 1/3 used to precondition converter gases prior to hot ESP. Any excess is solar evaporated on slag dump. No discharge.
3	0[a]	Blowdown from packed tower used in open tower blowdown to clarifier. One-half recycled to packed tower, other half to two-stage ammonia neutralization facility. Then 2.2 ℓ/sec to converter hot ESP for gas preconditioning and 0.6 ℓ/sec to hot ESP for gas preconditioning (joins 0.6 ℓ/sec DMA purge). No discharge.
4	0	Blowdown to tailings pond. Pond water recirculated to mill concentrator. No discharge.
5	0	Blowdown from new scrubbers and mist precipitators to recycle and tailings thickener underflow. No discharge.
6	0	Blowdown used in mill concentrator circuit. No discharge.
7	0	Blowdown to settling pond and either recycled or wasted. No discharge.
8	0	Blowdown to acid ponds and reused in copper precipitation leach facility. No discharge.
9	0[a]	Blowdown currently used to blend fluid-bed roaster feed. Anticipate closed circuit, but will eventually send to proposed treatment facility.
10	3.4 ℓ/sec	Blowdown to lime pond, then to tailings pond. Eventual (8 km of ponds) discharge.
11	50-190 ℓ/sec[a]	Blowdown to go to new treatment facility with subsequent discharge.

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[a] Anticipated, practice under construction.

Source: PE-274

scrubbing column. The gases are then released to a stack. The SO_2 is desorbed from the DMA with steam and recovered as dry, 100 percent sulfur dioxide, which is compressed, cooled, and stored as a liquid while the DMA is recovered for recycling.

Scrubbing the gas stream in a weak sulfuric acid column produces a liquid waste blowdown stream similar to that from a sulfuric acid plant. Normally, however, the same scrubber is used to treat gases that feed both the acid plant and DMA plant. This stream could be neutralized and recycled as coolant to a hot ESP unit, thus returning the metals content to metallurgical processing.

A liquid waste continuously purged from the DMA process consists of water, sodium sulfite or bisulfite, and sodium sulfate. The quantity is about 18 kilograms per metric ton of SO_2 produced, when treating gas with 5 percent SO_2 content (PE-274). The stream typically contains about 4.5 percent dissolved solids, 25 mg/ℓ DMA, and 18 mg/ℓ suspended solids, with a pH around 5.8 (PE-274).

This purge stream is the only waste of this character generated by the primary copper industry. It is a clear stream with a BOD and a COD and is quite concentrated with nonrecoverable minerals. Each of the three operating DMA plants treat the purge stream differently. One adds it to the concentrator circuit; one mixes it with the acid plant blowdown, which is in turn sent to a hot ESP unit; the third uses activated carbon to absorb the DMA content, then uses it as part of a fluid-bed wet feed blending, which returns it directly to the metallurgical processing.

Arsenic Recovery--

Most of the arsenic present in a copper ore concentrate will be volatized in either the roasting or smelting processes. Some will escape into the atmosphere with the roaster or reverberatory furnace flue gas. Some arsenic will appear in the dusts collected from the electrostatic precipitators and other particulate removal equipment. One smelter with a high arsenic concentration in their feed material treats those dusts to extract arsenic for sale. Since demand for arsenic is small, this smelter satisfied most of the United States demand. As a result, effluent streams for this process are specific for only one site.

The collected dusts are charged to a Godfrey roaster and are heated until the arsenic vaporizes. The vapors are condensed in chambers, and are then resublimed and condensed to yield an arsenic trioxide product more than 99 percent pure. Arsenic metal is also produced by reacting arsenic trioxide with carbon in a reducing atmosphere.

The washdown from this arsenic recovery plant is mixed with another waste stream and is discharged to a pond. Table 23 indicates that up to a kilogram of arsenic may enter the pond each day from this source.

TABLE 23. ANALYSIS OF ARSENIC PLANT WASHDOWN WATER

Parameter	Concentration mg/ℓ
As	310.0
Cu	88.4
Zn	37.0
Pb	7.7
Cd	1.05
Hg	0.0003
Se	0.04
Te	0.43
Ni	0.75
Fe	9.4
$SO_4^=$	340.0
CN^-	0.01
Oil and Grease	0.04
pH	3.8 to 4.4

Fire Refining and Anode Casting--

Impure or "blister" copper from the converters must be refined to remove impurities. This is partially accomplished by fire refining, the last major process that occurs at a copper smelter.

Blister copper is placed in a fire refining furnace, a flux is usually added, and air is blown through the molten mixture. Most of the remaining sulfur oxidizes, some impurities vaporize, and other impurities oxidize and are removed in the slag. The excess oxygen in the mixture is then removed by either blowing reformed gas into the molten metal or by forcing wooden poles under the surface of the melt. The copper is then poured into molds and cooled with water sprays or by immersion in a tank of water. The resulting anodes are sent to an electrolytic refinery for further processing.

Water used for direct (contact) cooling of the casting machine and the copper anodes is usually a recirculated stream or is reclaimed water from combined sources. Table 24 shows the water consumption for five smelters. The water used for anode cooling is reported to pick up additional amounts of arsenic, copper, zinc, and also aluminum and chlorides, probably from mold dressing compounds. Table 25 lists the difference between inlet and outlet concentrations reported for one anode cooling operation. Table 26 lists the controls of contact cooling water being practiced by the domestic smelters including water used for cooling of both anodes and blister copper direct from the converter.

Electrolytic Refining--

Electrolytic refining reduces the total impurities in copper to approximately 0.05 percent. The refining is done by passing a direct current of electricity through two copper electrodes that are immersed in a bath of acidic copper sulfate solution. The anode is a casting of impure copper from the smelter, and the cathode is a "starting sheet" of refined electrolytic copper. The electric current causes the copper to dissolve from the anode and deposit at the cathode. Impurities collect either as slimes in the bottom of the cell or as soluble ions in the electrolyte.

Water is used for washing the electrodes as they are removed from the cells. This is usually steam condensate, since untreated water contains minerals that affect the quality of the product. This same water is used for make-up to the electrolyte system to replace that lost in purge and evaporation.

Most refineries reclaim the copper from spent electrolyte, but two do not, and therefore create a substantial liquid waste directly from the electrolytic cells. Table 27 lists the composition ranges for the electrolyte solution, the refined copper, and the slime that is recovered from the bottom of the cells. Leaks, spills, and occasional major discharges frequently are not included in these tabulations. One refinery that does not reclaim the spent electrolyte solution treats this stream by placing it in a lined pond and allowing it to evaporate to dryness. Dry climatic conditions make this possible. The other refinery mixes it along with other wastes and

TABLE 24. WATER REQUIREMENTS FOR COPPER REFINERIES

Plant	Water intake, liters per metric ton of metal producted	Water consumed (Intake minus discharge), liters per metric ton metal producted
A	4,000	4,000
B	9,000	700
C	13,000	1,200
D	3,000	1,900
E	6,000	0

TABLE 25. WASTE EFFLUENTS FROM ANODE COOLING WATER

Parameter	Net change, mg/ℓ	Net loading	
		kg/day	kg/metric ton
Chloride	8.7	7.8	0.029
Aluminum	0.12	0.11	0.0004
Arsenic	0.01	0.01	<0.0001
Copper	8.53	8.07	0.030
Zinc	0.25	0.24	0.0009
Flow, 10^6 ℓ/day	0.95		
Production, metric ton/day	265.0		

TABLE 26. CONTACT COOLING WATER CONTROL AND TREATMENT PRACTICES

Plant code	Discharge	Control and/or treatment practice
1	0	Anode casting: water in closed circuit with cooling tower, cooling tower blowdown joins blowdown from wire-bar casting cooling tower blowdown, entire blowdown to side-stream filter, anticipate total water recycle.
2	0	Anode casting: water directly reused in mill concentrator circuit. No discharge.
3	0	Anode casting: water collected in mill tailings thickener, all flow recycled (with some evaporation) to mill concentrator. No discharge.
4	0	Blister cake cooling: air cooled with some water spray; spray water totally recycled from cooling pond. No discharge.
5	Intermittent	Fire-refined (cathode) - shape casting; water mostly recycled, with small intermittent discharge.
6	0	Fire-refined casting: water to thickener, verflow recycled. No discharge.
7	0	Anode casting: water in closed circuit with cooling tower, blowdown to evaporation pond. No discharge.
8	0	Anode casting: water in closed circuit with cooling tower, blowdown reused in mill concentrator. No discharge.
9	0	Anode casting: water to tailings thickener, reused in mill concentrator. No discharge.
10	0	Anode casting: water all used in mill concentrator circuit. No discharge.
11	0	Anode casting: water in closed circuit with 100 percent circulation. No discharge.
12	5670 m^3/day	Anode casting: water collected in slag settling pond, part is recirculated for slag granulation 53,000 m^3/day. Remainder 5700 m^3/day discharged to tailings ponds. Eventual (8 km of ponds) discharge.
13	18 ℓ/sec	Anode casting: once-through water, part used for shot copper cooling, remainder discharged.
14	$\sim$340 m^3/day (125 ℓ/sec, 45 min/day)	Shot copper cooling: Intermittent flow, all discharged. Plan to treat water in proposed treatment facility with anticipated discharge.
15	0	Blister cake cooling: water consumed during spraying and air cooling. No discharge.

Source: PE-274

TABLE 27. GENERAL RANGE ANALYSIS OF ELECTROLYTE, REFINED COPPER, AND ANODE SLIME

Constituent	Electrolyte, g/ℓ	Refined copper, %	Raw slime, % (dry basis)
Sulfuric	170-230		
Copper	45-50	99.95	20-40
Oxygen		0.03-0.05	
Sulfur		0.001-0.002	2-6
Arsenic	0.5-12.0	0.0001-0.001	0.5-4.0
Antimony	0.2-0.7	0.0002-0.001	0.5-5.0
Bismuth	0.1-0.5	0.00001-0.00002	tr.
Lead		0.002-0.0010	2.0-15.0
Nickel	2.0-20.0	0.0001-0.002	0.1-2.0
Selenium		0.0003-0.001	1.0-20.0
Tellurium		0.0001-0.0009	0.5-8.0
Gold		0.68-0.242[a]	1,714-10,286
Silver		1.71-17.1[a]	34,285-274,283
Platinum		tr.	N.A.
Palladium		tr.	N.A.
Iron		tr.	0.1-0.2

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[a] g/metric ton.

tr. = trace

N.A. = Not available

discharges it into a tailings pond, where lime is added to neutralize the acid. This refinery is also in an arid section of the country. Both refineries report no discharge into public waters.

Electrolyte Purification--

Impurities accumulate in the electrolyte solution in an electrolytic refinery. If a portion of the electrolyte is not removed from the circulating stream, these impurities will begin to deposit with the refined copper. In most cases, the purge stream is processed to recover the metal value.

All but two of the refineries in this country remove the copper from the purge stream. This is done in special "liberator" electrolytic cells that use insoluble lead anodes and sheets of copper as cathodes. The copper and frequently some of the impurities deposit on the cathode. The plates of copper return to the metallurgical processing either within the refinery or in the smelter, depending on quality. Some of the remaining impurities collect in the liberator cells as a sludge.

A few refineries recover a portion of the sulfuric acid from the purge stream by use of dialysis equipment. The dialyzers provide a partial separation of the acid and produce a stream in which impurities are more concentrated. The acid is returned to the electrolyte circulation.

Effluent from the liberator cells or the dialysis equipment may be concentrated further by removing water in vacuum evaporators. Concentration of the acid produces a sludge, which has a high concentration of nickel sulfate and usually also contains iron and zinc. This sludge can be filtered out, and then part of the acid can be returned to the electrolyte system, or it may be discarded or sold.

Various smelters may practice all, part, or none of these treatments. Three refineries recover nickel. One refinery consumes all spent electrolyte in an associated chemical operation.

The waste streams for electrolyte treatment contain almost all the arsenic, antimony, and bismuth that comes in with the anode copper. Some of these elements may be returned to the smelter with liberator cathodes. Approximately a ton of arsenic may enter the electrolytic refinery with as little as 500 tons of anodes. Some of the arsenic is known to escape from the second stage of the liberator cells as arsine (AsH_3). Unless these elements are returned to the smelter with the liberator cathodes, antimony, and bismuth will exit with a purge of electrolyte acid. This waste stream is called "black acid."

In some refineries evaporated water from the electrolyte constitutes another waste stream, which usually is mixed with volumes of steam condensate and direct cooling water in barometric leg discharge devices. Table 28 provides an analysis from such a source.

TABLE 28. WASTE EFFLUENTS FROM $NiSO_4$ BAROMETRIC CONDENSER

Parameter	Intake, mg/ℓ	Discharge, mg/ℓ	Net change, mg/ℓ	Net loading, kg/day
pH	6.5	6.6		
Alkalinity	90.0			
COD	750.0	450.0	neg	
Total Solids	21,080	24,000	2,920	
Dissolved Solids	21,060	24,000	2,920	
Suspended Solids	18	18		
Sulfate (as S)	1,722	1,060	neg	
Arsenic	<0.010	<0.010		
Cadmium	<0.20	<0.20		
Copper	<0.20	<0.20		
Iron	<0.50	1.30	<1.3	<15.0
Lead	<0.50	<0.50		
Nickel	<0.50	<0.50		
Zinc	<0.20	<0.48	<0.48	<5.4
Flow, 10^6 ℓ/day		11.4		
Production, metric ton/day		415.0		

Melting and Casting Cathode Copper--

Refined electrolytic copper is either sold or melted and recast into shapes required by fabrication industries. There is usually also a final adjustment of the oxygen content of the finished product. Equipment used for these operations ranges from direct-fired reverberatory furnaces to continuous casting machines. Electric arc and induction furnaces may be used to melt or hold the molten copper.

Both contact and noncontact cooling waters are used to cool the casting equipment and the cast shapes. One refinery reports a water usage of 320,000 liters per day. Table 29 lists an analysis of water used for cooling the refined copper shapes at two refineries. Water from this process is often cooled prior to discharge, but is not usually specially treated.

Doré Metal Separation--

Doré metal, a mixture of silver, gold, and the platinum group metals, is separated into specification grades of each metal in a series of chemical and electrochemical laboratory operations. A special small electrolytic cell, the Moebius cell, is used to separate the silver, which is further processed to produce bullion bars of 1000 troy ounces each, analyzing 99.97 percent silver. Mud from the Moebius cell is melted into anodes and processed in another special electrolytic device, the Wohlwill cell, which produces gold of marketable quality. The remaining electrolyte is chemically processed to separate platinum, palladium, and occasionally iridium, rhodium, ruthenium, and other metals.

Wastes are insignificant in comparison to other processes. No losses of metallic elements occur in this process. There are minor evolutions of nitrous oxides, sulfuric acid mists, and other acid fumes, and occasional liquid discharges of electrolyte acids in quantities of a few gallons at most.

Heap and Vat Leaching--

Heap and vat leaching are simple forms of hydrometallurgy, in which valuable metals are dissolved from ores to form water solutions. In heap leaching, the ores are placed in a dump, or pile, on the ground. In vat leaching, they are placed in tanks, with or without pretreatment.

Heap leaching is usually applied to low-grade ore and mine overburden that contains less than 0.4 percent copper. The ore is placed in an area provided with drainage ditches and basins, and is flooded with sulfuric acid solution and then allowed to drain. The copper minerals react to form soluble copper sulfate which washes from the heap with the acid solution. From 70 to 82 percent of the copper in these low-grade ores can be recovered. The liquor that seeps from the heap has a pH of 1.5 to 2.5 and may contain from 1.0 to 18 grams of copper per liter (PE-274).

Vat or percolation leaching is applied to oxidized copper minerals, which occur as partially weathered deposits in the mine. These minerals

TABLE 29. ANALYSIS OF WATER USED TO COOL REFINERY SHAPES
(Concentrations in mg/ℓ)

Parameter	Plant X		Semicontinuous cake casting	Plant Y	
	Inlet water	Wirebar cooling		Inlet water	Wirebar cooling recycle
pH	7.6	7-8	8.0	7.1-7.6	8.0-8.4
TDS	1430.0	1250.0	1400.0	0.2	0.1
TSS	0.0	12.5	0.0	0.5	0.4
SO_4	240.0	240.0	270.0		
As	0.001	0.001	0.001	0.001	0.001
Cd	0.001	0.001	0.001	0.0008	0.0021
Cu	0.30	0.69	0.18	0.021	3.5
Fe	0.02	0.13	0.04	1.2	1.7
Pb	0.007	0.007	0.003	0.078	0.068
Hg	0.00350	0.00425	0.0001	0.00004	0.00004
Se	0.001	0.001	0.001	0.040	0.040
Te					
Zn	0.001	0.067	0.001	0.35	0.088
Oil and Grease	0.0	2.0	0.0	0.14	0.1

cannot easily be reclaimed by conventional flotation processes. They are selectively mined and are placed in concrete vats where they are subjected to alternate flooding with sulfuric acid and draining.

The leaching liquor eventually becomes so rich in iron that it must be discarded. The volume is reported as varying from 350,000 to 1,000,000 liters of spent liquor per metric ton of copper produced but no effluent analyses have been reported. Most installations mix the discharge of this process with mining or concentrating wastes.

Solvent Extraction--

Solvent extraction is used to produce a concentrated copper solution from a solution of copper that contains other dissolved metals. When organic solvents are mixed with the impure solution, the copper complexes with the solvents. The solvents containing the copper form a separate phase from the aqueous phase containing the impurities. The organic layer is removed and mixed with sulfuric acid. This breaks down the complex and regenerates the solvent for reuse. The copper is withdrawn as a solution in the acid.

The concentrated acid solution can be directly treated by electrowinning. It is likely that there will be a bleed of the concentrated acid to prevent accumulation of these other elements. The loss of solvent is reported as 1 liter per 10,000 liters of raffinate. This loss is probably kerosene, which has a slight water solubility. The more expensive chelating compounds should stay largely dissolved in the kerosene layer. The acid blowdown should be of a quality that could be reused in other processes. The organics lost in this waste stream should be biodegradable.

Electrowinning--

Electrowinning is similar to the cells of an electrolytic refinery, except that an inert anode is used. Relatively pure copper metal is extracted from a solution containing copper ions. Copper metal deposits at the cathode, and the water in the solution is electrolytically decomposed, liberating oxygen at the cathode, and generating the sulfate ion as sulfuric acid.

The copper produced by electrowinning is comparable to electrolytic copper, assaying 99.9+ percent, if the copper solution is relatively pure. If impure solutions are used, the purity is equivalent to that of the anode copper from a conventional smelter and the product requires electrolytic refining prior to sale.

No data is available on the characteristics of the small amount of liquid waste discharged as a result of cathode washing.

PRIMARY LEAD INDUSTRY

Industry Description - Primary Lead

The United States primary lead industry consists of six smelters and five refineries. Four sites have both smelting and refining. Two sites have only smelting operations and ship their bullion to another site for refining.

Mining, concentrating, smelting, and refining are the four major phases of lead processing. Lead is mined from lead sulfide ore which typically contains 3 to 8 percent lead by weight. In certain areas in Missouri, ore containing up to 70 percent lead is being mined. Ore is processed in a series of crushing, grinding, classifying, flotation, and float-sink steps to produce a concentrate containing 55 to 70 percent lead by weight. The pyrometallurgical steps in lead smelting are preceded by charge preparation and pelletizing steps which actually lower the lead concentration of the feed concentrate to 30 to 45 percent. Fluxes, coal, limerock, and return slag are added to insure proper pelletization and good combustion during sintering.

Prior to 1963, lead ore mined in the United States typically contained 3 to 8 percent lead by weight and contained zinc, iron, nickel, and copper impurities. In 1963, lead ore containing as much as 70 percent lead was discovered in Missouri. In some places the ore is pure galena. This ore contains smaller concentrations of impurities than ore in the older mines.

Lead ore from the older mines requires dressing or milling before smelting. Standard grinding and flotation techniques concentrate the lead from the 3 to 8 percent level found in typical ores to 45 to 70 percent. Common flotation chemicals are Na_2CO_3, CaO, $CuSO_4$, xanthate, pine oil, cresylic acid, and NaCN. The product lead concentrate is dewatered, thickened, and filtered before being sent to the smelter. At this point, the concentrate contains 6 to 15 percent zinc, 5 to 15 percent iron, 13 to 18 percent sulfur, and minor amounts of cadmium, gold, silver, magnesium, manganese, arsenic, and antimony (MC-004, KI-048).

The lead smelting phase involves concentrate preparation and pelletizing, sintering, and reduction in a blast furnace. Feed concentrates for smelting must be carefully blended with high silica lead ores, by-products, return sinter, and fluxes to insure complete mixing before being stored in bedding piles. The bedded charge is normally conditioned to adjust moisture content to 6 to 8 percent. The charge is then pelletized in a gas or oil fired rotary pelletizer which maintains the exit gas temperature at 600°F (KI-048). The pellets (1/8 to 3/16 in.) are then stored as sinter machine feed.

Prepared concentrate is sintered to remove volatiles, to oxidize lead sulfide, and to produce a charge with enough structural strength to be suitable for direct feed to a blast furnace. In the sintering step, a conditioned, pelletized charge is ignited on a traveling metal grate. Metallic sulfates and sulfides in the charge are oxidized to metallic oxides, volatiles are driven off, and a suitable blast furnace charge or "clinker" is produced.

The clinker is broken as it comes off the end of the traveling grate. It is then charged to a blast furnace with coke, fluxes, and recycled drosses (normally metal oxides) for reduction.

After the sinter and coke are charged to the blast furnace, reaction heat is provided through coke combustion by blowing air through tuyeres located near the bottom of the blast furnace shaft.

The blast furnace reduces the lead oxides formed during sintering to metallic lead and CO. Four molten layers may form in the blast furnace. Lead will sink to the bottom of the blast furnace shaft. A layer of speiss (antimonides and arsenides of iron and other metals with a specific gravity of 6.0) will float on the lead. Matte (copper and other sulfides with a specific gravity of 5.2) will form above the speiss, and slag (silicates with a speccific gravity of 6.0) will form the upper layer. Lead bullion is tapped from the blast furnace and is either sold as antimonial lead or further refined. Impurities (mainly iron and zinc) accumulate in the slag and are sent to a slag fuming furnace.

Refining lead bullion may be accomplished pyrometallurgically or electrolytically. Refining involves the step-wise removal of impurities including copper, antimony, gold, silver, zinc, and cadmium. These impurities are normally sold as secondary products of lead refining. Refined lead is sold as soft, semisoft, or hard lead depending on the impurities it contains. Soft lead is 99.9+ percent pure. Semisoft lead contains 0.3 to 0.4 percent antimony, and up to 0.05 percent copper. Hard (antimonial) lead is typically 5 to 12 percent antimony, 0.2 to 0.6 percent arsenic, 0.5 to 1.2 percent tin, 0.5 to 0.15 percent copper, and 0.001 to 0.01 percent nickel (DA-069). Other impurity elements are often substituted to maintain equivalent physical properties.

The first refining step is drossing to remove copper. The copper in the dross is recovered in a reverberatory furnace and the reverb slag is recycled to the blast furnace. Decopperized bullion is then treated in a "softening furnace" which removes antimony, arsenic, and tin, the elements which make lead hard.

Gold and residual copper are removed by adding zinc dust to the molten bath to form a zinc-copper-gold crust. Zinc is again added after the gold crust is skimmed and a silver-zinc crust forms and is skimmed off. Zinc is removed by reaction with chlorine or by vacuum distillation. Bismuth is removed in a refining kettle by adding calcium and magnesium. Electrolytic refining may follow any of the above refining steps depending on the type of lead and secondary product desired.

Wastewater Source Identification - Primary Lead

Table 30 lists each of the processes in the primary lead industry for which effluent streams have been identified. Unlike the copper industry, most lead mines, concentrators, smelters, and refineries are located in areas where rainfall exceeds evaporation. Surface evaporation of wastewaters is not

TABLE 30. SUMMARY OF POLLUTANTS IN INDUSTRIAL WASTEWATER SOURCES - PRIMARY LEAD

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)		Ref.	Comments
Primary Lead Industry					
Mining					
- Mine drainage	(seasonal)		Range of Five Missouri Mine Water Samples	PE-274	Water from Missouri mines is alkaline, while drainage is acidic, requiring neutralization.
		pH	7.8 - 8.1		
		Cu	0.004-700.0		
		Pb	0.020-0.065		
		Zn	0.008-0.036		
		Mg	12.0 -15.0		
		Ca	27.0 -30.0		
		Na	32.0 -54.0		
		K	3.0 -4.2		
			Other Constituents	PE-274	
		Hg	0.001-0.002		
		Cd	<0.002-0.058		
		Cr	<0.010-0.17		
		Mn	<0.02 -57.2		
		Fe	<0.02 -2.5		
		Sulfate	63.5 -750.0		
		Chloride	<0.01 -57.0		
		Fluoride	0.063-1.2		
Concentrating					
- Tailings slurry from flotation or gravity separation	4 m^3/m ton ore processed	Hg	<0.001	PE-274	
		Pb	0.107-1.9		
		Zn	0.12 -0.46		
		Cu	0.014-0.36		
		Cd	0.005-0.011		
		Cr	0.002-0.02		
		Mn	0.03 -0.169		
		Fe	0.03 -0.53		

(Continued)

TABLE 30 (Continued)

<table>
<tr><th>Source</th><th>Flow (ℓ/min)</th><th>Stream Composition (mg/ℓ)</th><th>Ref.</th><th>Comments</th></tr>
<tr><td><u>Primary Lead Industry (Cont'd)</u></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Contact Acid Plant</td><td></td><td></td><td></td><td></td></tr>
<tr><td>- Off-gas scrubber liquor (i.e., acid plant blowdown)</td><td>In one case 273 m³/day is discharged.*</td><td>See composition reported for contact acid plant in Primary Copper.</td><td>PE-274</td><td>Similar to effluent from acid plant in primary copper industry.
*Other plants combine with other effluents for treatment or use in slag granulation.</td></tr>
<tr><td>Blast Furnace</td><td></td><td></td><td></td><td></td></tr>
<tr><td>- Slag granulation water*</td><td></td><td></td><td>PE-274</td><td>*Many plants now charge slag to slag fuming furnace rather than directly to slag granulation.</td></tr>
<tr><td>Slag Fuming</td><td></td><td></td><td></td><td></td></tr>
<tr><td>- Slag granulation water</td><td>6 million ℓ/day</td><td>
<table>
<tr><th>Parameter</th><th>Total plant intake mg/ℓ</th><th>Total plant discharge mg/ℓ</th><th>Net change, mg/ℓ</th></tr>
<tr><td>pH</td><td>7.6</td><td>8.3</td><td>-</td></tr>
<tr><td>Dissolved solids</td><td>408.0</td><td>500.0</td><td>92.0</td></tr>
<tr><td>Sulfate (as S)</td><td>145.0</td><td>215.0</td><td>70.0</td></tr>
<tr><td>Chloride</td><td>18.0</td><td>-</td><td>-</td></tr>
<tr><td>Calcium</td><td>70.0</td><td>-</td><td>-</td></tr>
<tr><td>Copper</td><td>0.02</td><td>0.02</td><td>0</td></tr>
<tr><td>Iron</td><td>1.70</td><td>-</td><td>-</td></tr>
<tr><td>Lead</td><td>0.12</td><td>0.30</td><td>0.18</td></tr>
<tr><td>Magnesium</td><td>0.31</td><td>-</td><td>-</td></tr>
<tr><td>Nickel</td><td>0.03</td><td>0.04</td><td>0.02</td></tr>
<tr><td>Zinc</td><td>0.05</td><td>0.12</td><td>0.38</td></tr>
</table>
Process water flow: 6 million liters/day (1.55 million gal/day).
Production: Metric tons/day (630 short tons/day).
Source: This contract and 1971 RAPP data.</td><td>PE-274</td><td></td></tr>
<tr><td>Final Refining and Casting</td><td></td><td></td><td></td><td></td></tr>
<tr><td>- Ingot cooling water</td><td></td><td></td><td>PE-274</td><td>Either recycled to slag granulation or discharged to tailings pond. Liming is sometimes practiced.</td></tr>
</table>

possible. Table 30 summarizes the available data on the characteristics of these process specific wastewaters. The following discussion describes the sources of these wastewaters in more detail.

Mining--

Most lead ore is obtained from underground mines. The ore is cut from the deposit, it is taken to the surface by rail, trackless shuttle cars, or conveyor belts and is then transported to ore concentrating facilities. Wastewater from lead mining results from seepage of surface water, interception of aquifers, runoff rom spoil dumps, and water sent into the mine for utility purposes. The water is pumped from the mine at a rate necessary to maintain mining operations. The required pumping rate is subject to seasonal variation and bears no relation to the ore output. The rate can range from tens to thousands of cubic meters per day.

The wastewater contains dissolved and suspended solids that reflect the composition of the ore being mined. Small amounts of oil and hydraulic fluid resulting from spills or leaks will also be present. A Missouri mine wastewater analysis is given in Table 31. The chemical characteristics are typical of those from any sulfide mine.

TABLE 31. ANALYSIS OF A MISSOURI MINE WATER

pH	Cu µg/ℓ	Pb µg/ℓ	Zn µg/ℓ	Mg mg/ℓ	Ca mg/ℓ	Na mg/ℓ	K mg/ℓ
7.8		65	8	13	30		
7.8	4	20	15	14	27	32	4.2
7.8	4	36	19	15	29	42	3.8
8.1	0.5	31	22	12	30	53	3.2
8.1	0.7	53	36	13	30	54	3.0

Other typical mine wastewater constituents and their concentrations are given below.

Component	Concentration, mg/ℓ
Mercury	0.001 to 0.002
Cadmium	<0.002 to 0.058
Chromium	<0.010 to 0.17
Manganese	<0.02 to 57.2
Iron	<0.02 to 2.5
Sulfate	63.5 to 750
Chloride	<0.01 to 57
Fluoride	0.063 to 1.2

Wastewater is generally treated by liming and impoundment as practiced in copper mining. Since water from Missouri mines is basic, liming may not be required for pH adjustment. Water from western lead mines is acidic and is treated in a fashion similar to water from copper mines. After treatment, the wastewater is normally reused in ore milling operations.

Concentrating--

The concentrating process is similar to the process described for copper ore concentrating. Except for high-grade galena ore produced in southeastern Missouri, ore concentration is required to produce feed material suitable for subsequent metal recovery processes. The process consists of milling the ore by crushing and grinding, followed by separation into two or more fractions. The fractions rich in desired minerals are called concentrates, and the fractions low in mineral content are called gangue.

Separation is achieved by both gravity and froth flotation methods. The gravity method achieves separation because of differences in specific gravity of the lead-rich minerals and the gangue particles. The flotation method achieves separation by the use of compressed air and chemical additives that create a froth in which finely divided mineral particles are floated from the gangue. The flotation method may serve as a supplement to gravity separation to improve the concentrate and is similar to copper ore flotation. Flotation is practiced chiefly by lead mines in the western United States.

Lead producers of the Mississippi Valley and the eastern United States use gravity separation because there is considerable difference in specific gravities of the ore minerals and the gangue. Since the milled ore particles need not be as small as those required for flotation, the milling costs are lower. Two modes of gravity separation are commonly used, jigging and float-sink. In jigging, the crushed ore particles are fed to an agitated, water-filled jigging chamber where the heavier ore particles gravitate to the bottom and the lighter gangue is displaced to the top and removed. The float-sink mode utilizes a liquid medium, such as an aqueous ferrosilicon suspension, with a specific gravity between that of the lead mineral and the gangue. The mineral particles sink, while the gangue floats to the top for removal by skimming.

The ore concentrates from the flotation cells are dewatered before shipment to smelters. Liquid waste from the concentrating operation is in the form of a tailings slurry discharged to the tailings pond. Approximately 4 cubic meters (1,060 gallons) of tailings slurry are discharged per metric ton of ore processed. Table 32 lists concentrations for a few metals in concentrator wastewater.

TABLE 32. LEAD MILL WASTEWATER ANALYSIS

Component	Concentration, mg/ℓ
Mercury	0.001
Lead	0.107 to 1.9
Zinc	0.12 to 0.46
Copper	0.014 to 0.36
Cadmium	0.005 to 0.11
Chromium	0.002 to 0.02
Manganese	0.03 to 0.169
Iron	0.03 to 0.53

Acid Plant--

The sintering machine produces the only lead smelter exit gases treated by sulfuric acid production. A detailed description of this process is given in Section 7, under Contact Sulfuric Acid Plant.

Liquid waste effluents are treated by liming and settling in cooling ponds. Overflows are recycled to slag granulation or discharged. Tables 33 and 34 give the treatments now practiced for control of acid plant blowdown and scrubber wastewaters, respectively, by the three primary lead smelters having acid plants.

Slag Fuming Furnace--

A slag fuming furnace is used to recover metal values otherwise lost in the slag. Slag is fed molten to the fuming furnace and pulverized coal is added to maintain reaction temperature. A reaction fume is generated that normally contains zinc, germanium, lead, cadmium, chlorine, and fluorine.

TABLE 33. WASTEWATER TREATMENT AT PRIMARY LEAD ACID PLANTS

Plant	Liquid Effluent Treatment	Discharge
1	Enters water treatment plant, limed, thickened, and filtered, and sent to reservoir for recycle.	0
2	Recycled to slag granulation.	0
3	Enters liming sump, then passed to lime bed, then to a cooling pond.	273 m^3/day (72,000 GPD)

TABLE 34. SCRUBBER WASTEWATER TREATMENT AT PRIMARY LEAD PLANTS

Plant	Treatment	Discharge
1	Enters water treatment plant, limed, thickened, filtered, and then sent to reservoir for recycling.	0
2	Recycled from a cooling tower.	0
3	Sent to a lime sump then to a settling pit. Most is recycled.	Undetermined

The fume is condensed and processed to recover the metal values. The lead fraction is recycled to the sintering process. A leaching step may be necessary to avoid the accumulation of chlorine and fluorine. A matte is sometimes separated from the slag in this operation for recovery of substantial amounts of copper and silver from the slag.

When fuming has subsided, the slag is dumped and cooled with water. The dumped slag and water used for granulation constitute the major waste stream from this process. The water-soluble portions of the slag are leached by the cooling water. Table 35 presents analyses of intake and outflow streams of water used for slag granulation.

Slag is conveyed with the granulating water stream to a dump or tailings pond for disposal.

Current treatment and disposal practices for slag granulation water are variable, as summarized in Table 36. Normally, it is desirable to recycle the water after cooling and clarification. A smaller stream is bled off to control buildup of water-soluble components. Using neutralization and clarification to treat this wastewater, the following effluent concentrations can be achieved.

Component	Concentration, mg/ℓ
Cadmium	0.5
Lead	0.5
Mercury	0.005
Zinc	5.0

These values are currently being met by five of the six lead smelters. The estimated cost of treatment is $2.68 per metric ton ($2.43 per U.S. ton) of lead produced (PE-274).

Final Refining and Casting--

Refined lead bullion from dezincing or debismuthizing is given a final purification and cast into ingots. The refined lead is fluxed with oxidizing agents to remove remaining impurities such as lead oxide and magnesium or calcium residues. After slag removal by skimming, the purified lead, assaying 99.999 percent purity, is reheated and cast into ingots or pigs. Most casting is performed by fully automated machines.

Water is used to cool the cast lead ingots by direct contact, at rates ranging from 300 to 1,500 liters per minute. Direct contact cooling water becomes contaminated with lead and lead oxides. Several methods are used to treat the contaminated cooling water. The water is either recycled for use in slag granulation or is sent to a tailings pond for settling of suspended solids. Lime precipitation may also be used for metals removal.

TABLE 35. WASTE EFFLUENTS FROM SLAG GRANULATION

Parameter	Total Plant Intake mg/ℓ	Total Plant Discharge mg/ℓ	Net Change, mg/ℓ	Net Loading kg/ton
pH	7.6	8.3	-	-
Alkalinity	203	186	-17	-
COD	8	8	0	0
Total solids	-	-	-	-
Dissolved solids	408	500	92	0.89
Suspended solids	3	36	33	.32
Oil and grease	-	-	-	-
Sulfate (as S)	145	215	70	0.67
Chloride	18	-	-	-
Cyanide	-	-	-	-
Aluminum	-	-	-	-
Arsenic	-	-	-	-
Cadmium	-	-	-	-
Calcium	70	-	-	-
Chromium	-	-	-	-
Copper	0.02	0.02	0	0
Iron	1.70	-	-	-
Lead	0.12	0.30	0.18	0.0018
Magnesium	.31	-	-	-
Mercury	-	-	-	-
Molybdenum	-	-	-	-
Nickel	0.03	0.04	0.02	0.00018
Potassium	-	-	-	-
Selenium	-	-	-	-
Silver	-	-	-	-
Sodium	-	-	-	-
Tellurium	-	-	-	-
Zinc	0.05	0.12	0.38	0.0037

Process water flow: 6 million liters/day (1.55 million gal/day).

Production: Metric tons/day (630 short tons/day).

Source: PE-274

TABLE 36. PRIMARY LEAD SLAG GRANULATION WASTEWATER TREATMENT

Plant	Treatment	Discharge
1	Sent to cooling pond.	8,230 m^3/day (2,200,000 gpd)
2	Sent to settling pit then to a cooling pond.	273 m^3/day (72,000 gpd)
3	Sent to settling pond and recycled.	0
4	Sent to two settling ponds in series.	Discharge is present but no quantities are available.
5	Sent to a slag pile.	No apparent discharge to surface. Leaching is not mentioned.
6	No data.	No data

PRIMARY ZINC INDUSTRY

Industry Description - Primary Zinc

The major product of the primary zinc industry is metallic zinc; the industry also produces zinc oxide, sulfuric acid, cadmium, and occasionally other chemicals such as zinc sulfate. For the purpose of analysis, the zinc industry is subdivided into segments: pyrometallurgical zinc production, electrolytic zinc production, zinc oxide production, and cadmium recovery. Production of other by-product compounds such as germanium, thallium, gallium, and indium is not considered as part of this industry because this is not done at primary zinc smelters.

Generally, ore is mined and concentrated at one location and then transferred to smelters for the production of zinc, zinc oxide, or both. Cadmium is normally recovered at smelters from collected dusts and slags with sufficient cadmium content. Direct zinc oxide production uses the same ore concentrate as metallic zinc production.

Zinc occurs naturally in many igneous rocks. The principal ore is sphalerite known as "zinc blende" which is a cubic crystal of zinc sulfide (ZnS). Sphalerite varies in purity (up to 67.1 percent zinc) and is dispersed in various concentrations in the ore. Zinc is normally mined in underground mines although some open pit zinc mines also exist.

Zinc mined in the United States comes primarily from underground mines in the form of sulfide ores. Ore is crushed and ground in standard jaw, gyratory, and cone crushers, then separated by flotation. Concentrates normally contain 50 to 60 percent zinc, approximately 7 percent iron, and about 30 percent sulfur. Zinc concentrate is then treated either electrolytically or pyrometallurgically to recover zinc metal. Both techniques require roasting of the concentrate prior to treatment. In the roasting step, any sulfur present as sulfide must be removed. If electrolytic processing follows roasting, some sulfur present as $ZnSO_4$ is desirable to compensate for losses in the electrolytic refining cells. Pyrometallurgical processing requires nearly complete or "dead roasting".

Smelting of zinc concentrates is accomplished by different techniques at the two United States smelters which use pyrometallurgical reduction processes. In the vertical retort process, concentrate is blended with various smelter recycle streams, pelletized, dried, and then roasted in flash roasters. The roasted concentrate or "calcine" is again mixed with recycle streams and pelletized before being sintered for final sulfur removal. Sinter is mixed with coal, clay, and sulfite liquor and pressed into briquettes. The briquettes are coked to give them the structural strength and reactivity required for charging to the vertical retort. The volatile matter in the coal aids in supporting autogenous combustion during the coking process.

Vertical retorts have rectangular cross sections and are 12 to 18 inches wide and 6 to 8 feet long. Walls are constructed of silicon carbide to help transfer heat to the charge from fuel which is fired on the outside of the retort. Inside the retort, ZnO and carbon from the coal or coke react to form Zn and CO. The zinc vaporizes and passes out of the retort with the CO to a condenser. The condensed liquid zinc is removed continuously and the CO is used as fuel to fire the retort.

The electrothermic process also requires drying, roasting, mixing, pelletizing, and sintering of the concentrate. However, the sinter and coke are fed directly to the electrothermic furnace where heating is accomplished with electrodes submerged in the charge. Zinc and CO leave the furnace as vapor. The zinc is condensed and removed, while the CO is burned in a preheater to heat the furnace charge.

Electrolytic processing of zinc involves the leaching of roasted concentrate with spent electrolyte to remove the soluble zinc oxide. The solution is filtered and processed through electrolytic deposition cells in which zinc is plated out of solution on aluminum cathodes.

Some nonsulfur bearing ore is processed by at least one zinc smelter. Since oxide ore is not amenable to flotation, it is reduced, vaporized, and oxidized in Waelz kilns. The ZnO is then sintered and combined with the processed sulfide ores for zinc or zinc oxide production. Lead and copper ores are also major sources of zinc.

Primary zinc requires little refining after reduction. What little refining is done is usually performed by fabricators prior to casting.

Liquid effluents can be classified as non-contact and contact. Non-contact water is used for cooling in heat exchangers. Contact, or process, wastewater is produced in operations such as scrubbing of roaster gas and reduction furnace gas, cooling of metal castings, cadmium production, and auxiliary air pollution controls. The primary pollutants are zinc, cadmium, lead, and small amounts of arsenic and selenium.

Table 37 lists each of the processes in the primary zinc industry for which effluent streams have been identified. Table 37 summarizes the available data on the characteristics of these process specific wastewaters. The following discussion describes the sources of these wastewaters in more detail.

Mining--

Most zinc is mined underground using open shrinkage, cut-and-fill, or square-set stopping methods. A few mines, particularly in early stages of operation, use open pit methods which are similar to those used in copper mining.

Mining consists of drilling, blasting, removing the broken rock and transporting it to a concentrator. Mining operations range from several hundred to about six thousand metric tons per day capacity.

TABLE 37. SUMMARY OF POLLUTANTS IN INDUSTRIAL WASTEWATER SOURCES - PRIMARY ZINC

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)		Ref.	Comments
Primary Zinc Industry					
Mining					
- Mine wastewater	Highly variable	Pb	P	PE-274	
		Zn	P		
Concentrating					
- Mill wastewater	1,000-16,000 m^3/day	Range for Five Mills		PE-274	
Tailings (underflow from flotation cell) Overflow from concentrate thickeners Filtrate from concentrate dewatering		pH	7.9 -8.8		
		Hg	<0.0001-0.1		
		Pb	<0.1 -1.9		
		Zn	0.12 -0.46		
		Cu	<0.02 -0.36		
		Cd	0.005 -0.011		
		Cr	<0.02 -0.67		
		Mn	<0.02 -0.08		
		Fe	0.05 -0.53		
		CN^-	<0.01 -0.03		
		Cl^-	21.0 -395.0		
		F^-	0.13 -0.26		
Horizontal Retorting					
- Gas washing water		Zn oxides	P	PE-274	
		Metal oxides	P		
		HC	P		
Vertical Retorting					
- Gas washing water		Zn oxides	P	PE-274	
		Metal oxides	P		
		HC	P		
Electric Retorting					
- Gas washing water		Zn oxides	P	PE-274	
		Metal oxides	P		
		HC	P		
Oxidizing Furnace		Same as above.		PE-274	
Zinc Melting and Casting					
- Casting cooling water				PE-274	
Cadmium Purification and Casting					
- Sponge wash water				PE-274	
- Casting cooling water				PE-274	

NOTE: P = present, but levels not quantified.

Mine wastewater results from infiltration of groundwater, water pumped into the mine for machines, hydraulic backfill operations, and infiltration of surface water. Geographical location rather than the quantity of ore mined normally determines the quantity of mine effluent. The water required to maintain operations may range from thousands to 160 million liters per day. This water is normally contaminated with dissolved metals and such impurities as blasting agents, fuel, oil, and hydraulic fluid.

Low quantities of water are usually needed in the zinc flotation process; mine-water effluent is used at many facilities as mill process makeup water. Mine water generated from natural drainage is reused in zinc mining and milling operations whenever possible. The mine water may pass through the process first, or it may be conveyed to a tailings pond from which it is conveyed for mill flotation with recycled process water. Discharge may result because of an excess of precipitation, lack of a nearby milling facility, or inability to reuse all of the mine wastewater at a particular mill.

Acid mine water is normally neutralized by the addition of lime and/or limestone. Combining mine water with mill tails in the mill tailings pond can be an effective treatment for acid mine water containing dissolved metals. The water may be further treated by lime-clarification and aeration.

Concentrating--

Zinc ore concentrating is similar to the processes described for lead and copper ore concentrating. This is necessary because mined sphalerite is seldom pure enough to be reduced directly for zinc smelting. The zinc-bearing ore is crushed and ground to a product typically 60 percent smaller than 325 mesh.

After blending, the ore is pumped to flotation cells as an aqueous slurry, where flotation agents are added. The zinc sulfide and sometimes lead, copper, and other metal sulfides are recovered in the flotation froth. Generally, zinc sulfide flotations are run at a basic pH (usually 8.5 to 11), and the slurry is periodically adjusted with hydrated lime, $Ca(OH)_2$ (PE-274). The tailings or gangue materials are sent to a tailings pond for treatment.

The metal concentrates are thickened in settling tanks and the slurry is fed to vacuum drum filters, which reduce the moisture content to approximately 10 to 20 percent moisture. Zinc concentrate contains about 55 to 60 percent zinc. Rotary dryers may be used to further reduce the moisture content of the concentrates to 2 to 5 percent moisture. Table 38 presents a typical zinc concentrate analysis.

Concentrator water requirement ranges from 330 to 1,100 m^3/metric ton of ore processed per day (PE-274). Mine water is usually used for the mills. Liquid waste streams from zinc mills vary in volume from 1,000 to 16,000 m^3/day or from 330 to 1,100 m^3 per metric ton (PE-274). The raw wastewater from a lead/zinc flotation mill consists of the tailings streams (usually the underflow of the zinc rougher flotation cell), the overflow from the concentrate thickeners, and the filtrate from concentrate dewatering, along with any housecleaning water.

TABLE 38. RANGE OF COMPOSITIONS OF ZINC CONCENTRATES

Constituent	Percent
Pb	0.85-2.4
Zn	49.0-53.6
Au	not iden.
Ag	not iden.
Cu	0.35
As	0.105-0.15
Sb	not iden.
Fe	5.5-13.0
Insolubles	3.4
CaO	not iden.
S	30.7-32.0
Bi	not iden.
Cd	0.24

Table 39 gives the raw and treated waste characteristics of five mills. None of these mills use total recycle. Feed water for the mills is usually drawn from available mine waters; however, one mill uses water from a nearby lake. These data illustrate the wide variations caused by ore mineralogy, grinding practices, and reagents.

Lime precipitation is often used for the removal of heavy metals from mill wastewater. Secondary settling ponds, clarifier tanks, or flocculating agents (such as polyelectrolytes) are used to enhance removal of solids and sludge before discharge.

Tailings pond water may be decanted and reused as either makeup water or process water. Some treatment such as secondary settling, phosphate or lime addition, pH adjustment, flocculation, clarification, or filtration is usually required before this decanted water can be reused.

Six lead or zinc ore concentrators now use settling or sedimentation pond system with a primary tailings pond and a secondary settling or "polishing" pond with pH adjustment for control of the concentrator discharge. Effluent concentrations are limited to the following average values (in milligrams per liter): copper = 0.05, mercury - 0.001, lead - 0.02, and zinc - 0.5 (PE-274).

TABLE 39. RANGES OF CONSTITUENTS OF WASTEWATERS AND RAW WASTE LOADS FOR FIVE SELECTED MILLS

Parameter	Range of concentration in wastewater mg/ℓ		Range of raw waste load: Per unit ore milled, kg/1000 metric tons		Range of raw waste load: Per unit concentrate produced, kg/1000 metric tons	
	lower limit	upper limit	lower limit	upper limit	lower limit	upper limit
pH	7.9	8.8				
Alkalinity	26	609	410	1,600	1,450	10,200
Hardness	310	1,760	460	4,700	2,290	32,500
TSS	<2	108	7	285	30	2,000
TDS	670	2,834	940	8,500	4,800	50,900
COD	71.4	1,535	6	4,800	30	50,000
TOC	11	35	6.35	130	30	580
Oil and grease	0	8	5	21	30	130
MBAS surfactants	0.18	3.7	0.236	13	2.05	60.7
Phosphorus	0.042	0.150	0.108	0.876	0.54	2.54
Ammonia	<0.05	14	0.064	26.4	0.32	185
Mercury	<0.0001	0.1	<0.00013	0.0026	<0.00168	0.130
Lead	<0.1	1.9	<0.127	6.9	<0.900	32.2
Zinc	0.12	0.46	0.089	17.2	0.62	86.0
Copper	<0.02	0.36	<0.026	0.158	<0.18	1.96
Cadmium	0.005	0.011	0.008	0.018	<0.18	8.85
Chromium	<0.02	0.67	<0.026	1.77	<0.18	1.36
Manganese	<0.02	0.08	<0.026	0.290	<0.45	10.0
Iron	0.05	0.53	0.064	1.16	0.012	0.198
Cyanide	<0.01	0.03	<0.013	0.109	0.091	0.509
Sulfate	295	1,825	130	4,800	1,260	33,700
Chloride	21	395	20	870	210	4,070
Fluoride	0.13	0.26	0.370	0.944	203	5.45

[a] Value in pH units.

Vertical Retorting--

The vertical retort process is a continuous reduction/volatilization method for producing high-purity zinc from zinc oxide by reduction with carbon at elevated temperatures in vertical silicon-carbide retorts. Vertical retorts are large, refractory-lined vessels with externally fired gas chambers. The furnaces consist of three major sections: the charge column, the reflux section, and the combustion-heating chambers. The retort is rectangular in general cross section, about 0.3 meter wide, 1.8 to 2.4 meters long, and 10.6 meters high, with a capacity of about 7.25 metric tons of zinc per retort per day. The coal or coke fed to the vertical retort provides the carbon used for direct reduction of zinc.

The charge to a vertical retort must be a hard sinter or briquette. The briquettes are coked in an autogeneous coking furnace in an operation that also drives off volatiles which serve as fuel.

Coked briquettes are fed to the charging extension at the top of each vertical retort without intermediate cooling. The charge is heated by gas in chambers surrounding the retort sidewalls. Incoming combustion air is preheated in recuperators by gases from the combustion chambers. The charge passes downward through the combustion or heating zone of the vertical retort. Heat produced in the combustion chamber is transferred through the refractory walls of the column to the charge. As the charge moves down through the retort, the zinc oxide reacts with carbon to form zinc vapors and carbon monoxide. Approximately 95 percent of the zinc vapor leaving the retort is condensed to liquid zinc. The residue, containing approximately 10 percent zinc, is removed at the bottom through an automatically controlled roll discharge mechanism into a quenching compartment, and is removed for further treatment.

A venturi scrubber is used to control particulate emissions from vertical retorts. The gas scrubbing water contains zinc and metal oxides, possibly hydrocarbons, various particulates (as suspended solids), and the corresponding products of hydrolysis. Only one smelter currently uses vertical retorts. This wastewater is unique to that site.

Electrothermic Furnace--

The electrothermic process overcomes the problem of external heating by using electrodes immersed in the charge for heating. The charge acts as a resistance to the potential applied across the electrodes. Some air is fed to the retort to allow formation of CO as in the vertical retort process and the reactions which occur are the same.

Electrothermic furnaces are vertical refractory cylinders 2.4 meters long by 11 meters high. Several sets of graphite electrodes protrude into the shaft, each top electrode being linked in a single-phase circuit with a bottom electrode located about 7 meters below and nearly opposite the first (KI-048).

The bottom of the furnace, which is supported by a refractory-faced water-cooled steel ring, terminates about 12 inches above a refractory covered rotating discharge table. This rotary table continuously withdraws some of the spent charge. A charge height detector controls the speed of the rotating table, usually to about 0.03 RPM (RP-208).

High-velocity impingement type scrubbers are used to clean gases from the condenser. The gas washing water contains the same impurities as in vertical retorting and is specific to the one site using electrothermic furnaces.

Oxidizing Furnace--

In the direct or American process for zinc oxide production, zinc vapor from sintering is immediately oxidized without being condensed. The grate-type furnace, rotary or Waelz kiln, and electrothermic furnace are the three types of furnaces used for this purpose in the United States. The feed is reduced to form zinc vapor which is then oxidized and collected as dust.

In the grate-type furnaces, the coal-sinter feed (usually as briquettes) is spread over grates (traveling or stationary), then the sinter is deposited on top of the fuel layer. Air is forced through the bed to support combustion. The zinc vapors are ducted to a combustion chamber, where oxidation occurs and the zinc oxide product is formed.

The Waelz kiln is a large diameter, long rotary kiln that can be used for production of pure zinc oxide. It is more commonly used to process residues. Zinc-bearing material and solid fuel are continuously fed to the kiln, which typically rotates 1 to 1.5 rpm. The heat required for reduction of the contained zinc is supplied by supplemental fuel. The vaporized zinc is ducted to a combustion chamber, where air is admitted and the vapor burned to form zinc oxide.

The St. Joe electrothermic furnace may be modified for use as either a metal or an oxide producer. Instead of a large "vapor ring" or bulge in the furnace barrel midway between the upper and lower electrodes, the oxide furnace has openings at four levels between the electrodes, through which the evolved zinc vapor and carbon monoxide exit the charge. Coke and zinc-bearing sinter are continuously preheated and fed to the furnace. The heat energy required for smelting is introduced through electrodes immersed in the charge.

Water effluents from these processes are not well documented.

Melting and Casting--

In this process, the zinc from an electrolytic or pyrolytic plant is melted and cast into a marketable form. Pyrolytic zinc is usually molten whereas stripped electrolytic zinc sheets must be melted. Induction or gas-fired heating is typically used. The molten zinc is cast into slabs on a casting machine or blocks in stationary molds.

Casting cooling water generally contains suspended solids and oil and grease consisting of metal oxides, mold washes, and lubricants from casting equipment.

Cadmium Purification and Casting--

Cadmium sponge is purified by melting it with a caustic flux, with distilling and perhaps redistilling, or redissolving the sponge with sulfuric acid and collecting the cadmium by electrolysis.

In pyrometallurgical processing, the dried cadmium sponge is first mixed with coal or coke and lime. It is then transferred to a conventional horizontal-type retort, where the cadmium is reduced and collected as molten metal in a condenser. For ultra-purity, the metal is distilled in graphite retorts. Thallium is removed by treatment with zinc ammonium chloride or sodium dichromate. The metal may then be cast into a marketable form or further purified by redistillation.

Electrolytic processing of cadmium is carried out in banks of cells similar to zinc cells. The sponge is dissolved in dilute sulfuric acid (return electrolyte). The anodes are lead. The cathodes of cadmium are 97 percent pure and represent 90 to 95 percent total recovery of cadmium from ore to metal. Recovery in the electrolytic step is 96 percent from the cadmium sponge. The stripped cathode metal is washed, dried, and melted under a flux, such as caustic or rosin, and cast into various shapes.

Water effluent streams from this process are not well characterized. Quantities should be small and may contain Cd, HCl, Tl, $ZnNH_3Cl$, and organics.

SECONDARY COPPER INDUSTRY

Industry Description - Secondary Copper

The secondary copper industry utilizes copper-bearing scrap to produce metallic copper and copper based alloys. For the purposes of this discussion, brass and bronze will be considered to be products of the secondary copper industry due to similarities in the operations and an overlap in the population of companies producing secondary copper, brass, and bronze. The processes used in this industry include scrap pretreatment, melting, alloying, refining, and casting.

According to an extensive industry survey published in 1973 (NA-182), there were 44 companies producing secondary copper, brass, and bronze products. A more recently study identified forty-five secondary copper, brass, and bronze smelters. The majority of this industry's production is concentrated in the northeast quadrant of the country.

The raw materials used by this industry can be classified first as new scrap (66 percent), i.e., produced in the fabrication of finished products, or old scrap (34 percent), from obsolete, worn out or salvaged articles

(US-357). Old scrap sources include wire, plumbing fixtures, electrical machinery, automobiles and domestic appliances. Other materials with copper values include slags, drosses, foundry ashes and sweepings from smelters and copper processing industries. The sources of recovered copper were 870,464 short tons of new scrap and 441,841 tons of old scrap (SC-303).

A tabulation of the compositions of various standard brasses and bronzes is given in Table 40. This table gives the composition of both raw materials and products for secondary brass and bronze processors. Although specifications for scrap impurities such as wire insulation, oil, grease, and paint are not given, these materials often contribute to the potential effluents associated with processing.

TABLE 40. NOMINAL CHEMICAL SPECIFICATIONS FOR BRASS AND BRONZE INGOT INSTITUTE STANDARD ALLOYS

Alloy No.	Classification	Cu,%	SN,%	Pb,%	Zn,%	Fe,%	Al,%	Ni,%	Si,%	Mn,%
1A	Tin bronze	88.0	10.0		2.0					
1B	Tin bronze	88.0	8.0		4.0					
2A	Leaded tin bronze	88.0	6.0	1.5	4.0					
2B	Leaded tin bronze	87.0	8.0	1.0	4.0					
2C	Leaded tin bronze	87.0	10.0	1.0	2.0					
3A	High-lead tin bronze	80.0	10.0	10.0						
3B	High-lead tin bronze	83.0	7.0	7.0	3.0					
3C	High-lead tin bronze	85.0	5.0	9.0	1.0					
3D	High-lead tin bronze	78.0	7.0	15.0						
3E	High-lead tin bronze	71.0	5.0	24.0						
4A	Leaded red brass	85.0	5.0	5.0	5.0					
4B	Leaded red brass	83.0	4.0	6.0	7.0					
5A	Leaded semi-red brass	81.0	3.0	7.0	9.0					
5B	Leaded semi-red brass	76.0	2.5	6.5	15.0					
6A	Leaded yellow brass	72.0	1.0	3.0	24.0					
6B	Leaded yellow brass	67.0	1.0	3.0	29.0					
6C	Leaded yellow brass	61.0	1.0	1.0	37.0					
7A	Manganese bronze	59.0	1.0	1.0	37.0	1.0	0.6			0.5
8A	Hi-strength mang. bronze	57.5			39.0	1.0	1.0			1.5
8B	Hi-strength mang. bronze	64.0			24.0	3.0	5.0			3.5
8C	Hi-strength mang. bronze	64.0			24.0	3.0	5.0			3.5
9A	Aluminum bronze	88.0				3.0	9.0			
9B	Aluminum bronze	89.0				1.0	10.0			
9C	Aluminum bronze	85.0				4.0	11.0	2.0		0.5
9D	Aluminum bronze	81.0				4.0	11.0	4.0		3.0
10A	Leaded nickel brass	57.0	2.0	9.0	20.0			12.0		
10B	Leaded nickel brass	60.0	3.0	5.0	16.0			16.0		
11A	Leaded nickel bronze	64.0	4.0	4.0	8.0			20.0		
11B	Leaded nickel bronze	66.5	5.0	1.5	2.0			25.0		
12A	Silicon bronze	88.0			5.0	1.5			4.0	1.5
12B	Silicon brass	82.0			14.0				4.0	

Source: NA-182

In addition to the scrap, other raw materials necessary for secondary copper processing include fluxes of boron minerals, old glass and salt; minor alloying components such as phosphorous, tin, and lead (if required); and leaching or reaction agents such as sulfuric acid and ammonium carbonate.

The classification system used to describe the various grades of recovered copper roughly corresponds to the various stages of the secondary refining process. In order of increasing copper purity, these grades of recovered copper are (NA-182):

1) "White metals" (babbit, lead, and solder) from sweating process. These may be used internally or sold to another processor.

2) Copper powder

3) Copper shot

4) Fire-refined copper

5) Electrolytic-refined copper

The products of the brass and bronze industry are hardeners and alloy ingots. There are 31 standard copper-base alloys produced by the members of the Brass and Bronze Ingot Industries.

Wastewater Source Identification - Secondary Copper

The secondary copper, bronze and brass industry is typical of the secondary nonferrous metals industry as a whole in that it is fragmented and difficult to characterize. Qualitatively, the various processes making up the industry are well known but hard data on process operating parameters and effluent characteristics are very limited. Consequently, the process descriptions in this section include many information gaps with respect to water effluents.

Aqueous waste streams come from three main sources: 1) liquid wastes from acidic or basic scrap leaching and dissolution processes, 2) waste cooling water from pouring and casting operations, and 3) liquid wastes and slimes from electrolytic refining. Much of the wastewater is either recycled or disposed of rather than being extensively treated. There should not be a serious problem if the ultimate long-term disposal is nonpolluting. The results of a survey of industry practices are given in Table 41.

For each process in this industry segment, aqueous effluents have been identified and characterized where possible. Table 42 lists each of the processes for which effluent streams have been identified and summarizes the available data on the characteristics of these wastewaters. The following discussion describes the sources of these wastewaters in more detail.

TABLE 41. SUMMARY OF WASTEWATER HANDLING PRACTICE AND DISPOSITION USED BY SECONDARY COPPER INDUSTRY

CONTROL PROCESS	NUMBER OF PLANTS (PERCENT) Brass and Bronze	Copper	Combined
No water use	1 (3)	0	1 (2)
No treatment, discharge to			
Stream	2 (6)	1 (14)	3 (7)
Sewer	8 (24)	0	8 (18)
Treat, discharge to			
Stream	1 (3)	1 (14)	2 (5)
Sewer	4 (11)	0	4 (9)
Recycled, no discharge	10 (29)	1 (14)	11 (25)
Recycled, some discharge to stream			
Periodic	3 (9)	2 (29)	5 (11)
Continuous	1 (3)	1 (14)	2 (5)
Recycled, some discharge to sewer			
Periodic	5 (14)	0	5 (11)
Continuous	2 (6)	1 (14)	3 (7)

Source: EN-378

TABLE 42. SUMMARY OF POLLUTANTS IN INDUSTRIAL WASTEWATER SOURCES - SECONDARY COPPER

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)		Ref.	Comments
Secondary Copper Industry					
Grinding and Gravity Separation					
- Blowdown from gravity separation recycle stream	72,000-3,000,000 ℓ/day		Range for 4 Plants	EN-462	For specific analyses, refer to Table 45.
		CN^-	<DL -0.163		
		Sb	0.111 -2.867		
		As	<0.02 -0.001		
		Cd	0.067 -1.683		
		Cu	0.071 -1250.0		
		Cr	0.12		
		Fe	0.007 -164.0		
		Pb	0.192 -917.0		
		Mn	0.05 -43.0		
		Hg	0.0003-0.002		
		Ni	0.030 -18.0		
		Zn	0.17 -983.0		
		pH	8.32 -9.8		
Insulation Burning					
- Scrubber blowdown					
Steam Distillation					
- Spent ammonium carbonate leaching solution	Intermittent				
Hydrothermal Hydrogen Reduction					
- Spent ammonium carbonate leaching solution	Intermittent				

(Continued)

TABLE 42 (continued).

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)	Ref.	Comments
Secondary Copper Industry (Cont'd)				
Blast Furnace/Reverberatory Smelting/Converter Smelting				
- Furnace cooling water				
- Ingot cooling and shot quenching water	18,200-605,600 ℓ/day	Range for 3 Plants	EN-378	Refer to Table 46 for specific analyses.
		CN$^-$ 0.057		
		Sb 0.01		
		As <0.02		
		Cd <0.05		
		Cr 0.02 -0.066		
		Cu 0.560-3.376		
		Fe 0.63 -1.8		
		Pb 0.5 -4.3		
		Mn 0.133		
		Hg <0.001		
		Ni 0.1		
		Zn 0.30 -17.8		
		pH 7.87 -8.9		
Electric Crucible Smelting				
- Metal cooling water		See above.		
Fire Refining				
- Metal cooling water		See above.		
Electrolytic Refining				
- Spent electrolyte			EN-378	The replacement rate for the electrolyte is as much as 75% a month. The blowdown is usually treated for metal value recovery before discharge. See Table 47.
- Slimes				
Electrolytic Winning				
- Spent electrolyte				Refer to Table 47.
- Slimes				
Electrolytic Powder Production				
- Spent electrolyte				Refer to Table 47.

Grinding and Gravity Separation--

This process accomplishes the same function as Shredding, but uses an aqueous separation medium and different input materials. The unit operations involved in this process are grinding, screening, and gravity separation. Their purpose is the concentration of the metal value in the scrap so that the subsequent thermal refining steps will not be overburdened with waste material.

A wide variety of materials with metal values are processed: a) slags, b) drosses, c) skimmings, d) foundry ashes, e) spills, f) sweepings and g) baghouse dust. These materials may be supplied by either an outside source or other processes at the secondary smelter.

The liquid waste stream would contain any soluble constituents of the gangue material, which encompasses a great variety of possibilities. Even if the water in the gravity separation step is recycled, there will be a blowdown/sludge stream which will create disposal problems. Examples of wastewater compositions are presented in Table 43.

Insulation Burning--

This process is intended to separate insulation and other coatings from copper wire by burning these materials in furnaces. The wire scrap is charged in batches to a primary ignition chamber. Combustion is started with auxiliary fuel and air. Volatile combustion products are then passed to a secondary combustion chamber or afterburner. Further treatment of combustion gases in a scrubber or baghouse is desirable if significant quantities of particulates or hazardous vapors are generated in this process. In most cases, the insulation burning is self-sustaining, but there can be problems with wire coated with polyvinyl chloride, fluorocarbon polymers or other flame resistant plastic formulations. If non-combustible inorganic materials such as fiberglass or ceramics are present they must be removed separately, either before or after burning.

The combustible portion of the wire scrap may include a considerable variety of materials, such as rubber, paper, natural and artificial fibers and fabrics, asphaltic materials or plastics such as polyethylene and polyvinyl chloride. Metallic and/or nonmetallic inorganic fillers may also be present. Plastics formulated for flame resistance may have bromine, phosphorus and antimony compounds up to levels of several percent by weight.

Liquid waste from this process consists of scrubber blowdown liquid. The nature of this material and hence the water treatment options required will be determined by the contaminants present in the furnace effluent gas stream.

Steam Distillation--

Copper is recovered from the leaching liquor of the ammonium carbonate process by steam distillation and precipitation as copper oxide. Copper as

TABLE 43. CHARACTER OF WASTEWATER FROM SLAG QUENCHING AND GRANULATION OR SLAG MILLING AFTER SETTLING

	Plant 9 - Net Loading[a]				Plant 11 - Gross Loading[b]				Plant 38 - Net Loading[b]				Plant 39 - Net Loading[b]			
	Intake	Discharge			Intake	Discharge			Intake	Discharge			Intake	Discharge		
	Conc., mg/l	Conc., mg/l	Loading kg/MT	(lb/ton)	Conc., mg/l	Conc., mg/l	Loading kg/MT	(lb/ton)	Conc., mg/l	Conc., mg/l	Loading kg/MT	(lb/ton)	Conc., mg/l	Conc., mg/l	Loading kg/MT	(lb/ton)
Product		Copper					Alloy				Alloy			Alloy		
MT/day		45.3					108				9.7			43.5		
(ton/day)		(50)					(119)				(10.7)			(48)		
Water flow																
l/day		3,000,000[c]				545,400				72,670			662,400	617,000		
(gal/day)		(792,000)				(144,100)				(19,200)			(175,000)	(163,000)		
Constituent																
Alkalinity	170	190	1.325	(2.650)	--	2965	14.976	(29.95)	71.33	104.67	0.250	(0.50)	685	733	0.681	(1.36)
COD	23.2	25.3	0.139	(0.278)	--				18.333	22.67	0.032	(0.064)				
Solids, Total	1294	1620	21.589	(43.18)	--	3900	19.695	(39.39)	421.3	6456	45.210	(90.42)				
Solids, diss.	64	336	18.013	(36.03)	--				387.67	2953.7	19.224	(38.45)	1,754	1,852	1.19	(2.78)
Solids, susp.	1231	1284	3.510	(7.020)	--	630	3.182	(6.364)	33.67	3502.3	25.986	(51.97)	21,405	22,980	326	(652)
TOC									63.3	268.67	1.539	(3.078)				
Phosphorus	0.029	0.031	0.0001	(0.0002)					0.293	0.403	0.001	(0.002)	1.0	1.0	NLC	
Cyanide	0.005	0.004	NLC[e]		--	NF[d]	--		0.053	0.163	0.001	(0.001)				
Antimony	0.142	0.111	NLC						<0.0	2.867	0.021	(0.042)				
Arsenic	0.001	0.001	NLC						<0.02	<0.02	NLC					
Boron	2.46	2.60	0.001	(0.001)					0.667	6.0	0.040	(0.080)				
Cadmium	0.111	0.067	NLC		--	0.11	0.0006	(0.0012)	0.067	1.683	0.012	(0.012)				
Copper	0.093	0.071	NLC		--	19.78	0.100	(0.20)	12	1250	9.275	(18.55)	0.10	0.11	0.00014	(0.00028)
Chromium						0.120	0.001	(0.002)								
Iron	0.005	0.007	NLC		--	13.0	0.066	(0.132)	1.833	163.667	1.212	(2.424)	13	14	0.0142	(0.0284)
Lead	0.297	0.192	NLC		--	23.0	0.116	(0.232)	5.333	916.67	6.835	(13.67)	0.9	1.0	0.0014	(0.0028)
Manganese	0.325	0.399	0.0005	(0.001)					0.467	43.33	0.321	(0.642)	0.05	0.05	NLC	
Mercury	0.0004	0.0003	NLC						<0.001	0.002	0.001	(0.002)				
Nickel	0.024	0.030	NLC		--	0.35	0.002	(0.004)	0.133	18.0	0.134	(0.268)				
Zinc	1.492	0.622	NLC		--	80.35	0.631	(1.262)	6.0	983.33	7.322	(14.64)	0.16	0.17	0.00014	(0.00028)
Oil and grease	1	1	NLC						11.0	23.333	0.092	(0.184)	0	0	NLC	
pH		8.32				9.8			7.4	8.53			9.35	9.35		

[a] Slag granulation.

[b] Slag milling.

[c] Estimated time for granulation 6 hr/day.

[d] NF = not found.

[e] NLC = no loading calculable.

Source: EN-462

cupric ion in an ammonium carbonate solution from the leaching process is the input material for this process. Boiling the solution precipitates the copper as the oxide. The steam distillation may take place at either atmospheric or higher pressures. This material is dried before it is sent to other processes such as hydrogen reduction or blast furnace/reverberatory smelting for copper recovery.

If the liquid waste is recycled to the leaching process, there is little potential for water pollution from this step. However, it is a potential wastewater source.

Hydrothermal Hydrogen Reduction--

As an alternative to the steam distillation the copper may be recovered from the ammonium carbonate leach solution by hydrothermal hydrogen reduction. Copper-containing ammonium carbonate solution containing 10 to 30 g/liter of copper is the input material. The heating of the liquor under hydrogen pressure precipitates the copper as a powder. The copper is filtered, washed, dried and sintered under a hydrogen atmosphere. The powder is then ground and screened. The spent liquor is recycled to the leaching process. The hydrogen reduction is carried out at a temperature of 160 to 225°C (325-400°F) and 3.58 megapascals (500 psig). The spent liquor is a possible liquid pollutant, but may be recycled to the leaching process.

Blast Furnace/Reverberatory Smelting--

This process uses equipment and techniques similar to primary copper ore smelting to produce black copper containing 70 to 80 percent copper for further refining. The feed is scrap of lower grade than that input to other secondary refining processes. The overall chemical process in the blast furnace is based on the reduction of copper by the coke fuel and the carbon monoxide formed from it. Impurities such as iron combine to form a slag which separates from the molten copper. The slag and metal mixture is tapped to a reverberatory furnace for separation.

The scrap is charged at the top of the blast furnace and proceeds downward, meeting reduced gases from the fuel at the bottom. The oxides of the base metals either dissolve in the slag, fume off, or are reduced and dissolve in the copper. The black copper product may contain zinc, lead, tin, bismuth, antimony, iron, silver, nickel, or other metals contained in the scrap. Sulfur in the coke or other feed materials reacts with the copper to form copper sulfide; this reaction can be largely avoided by using low-sulfur coke. The molten product may be cast into ingots or transferred in the molten state to a converter for further purification.

The scrap types normally charged to a blast furnace include high iron content copper and brasses, motor armatures, foundry sweepings, slags, drosses, and skimmings. It was then estimated in 1961 that the minimum profitable copper content was about 30 percent (SP-058). In 1973, it was reported that feeds containing as little as 10 percent copper can be processed economically (BU-184). Lower grade output of previous scrap preparation processes are used as inputs to the blast furnace.

The coke used as a fuel and reducing agent comprises about 10 percent of the charge. Limestone and millscale (iron oxides) are added to form an iron silicate slag for fluxing purposes.

The copper is maintained somewhat above its melting point of 1083°C (1981°F), usually in the range of 1090 to 1150°C (2000 to 2100°F). The slag leaves the furnace at about 1040°C (1900°F) (DA-069). A typical secondary blast furnace has a maximum diameter of 1.3 meters (50 inches), tapering to 1 meter (40 inches) at the top, with a water jacketed section 3 meters (10 feet) high. Air flow required is 38 to 46 $m^3/min/m^2$ of area at the bottom (125 to 150 $ft^3/min/ft^2$). The nominal capacity of such a unit would be in the range of 55 to 65 metric tons/day (60 to 70 short tons/day).

The coke charge supplies both process heat and acts as a reducing agent. Cooling water is also required by the furnace, and in the ingot casting and shot quenching operations.

The particulate emissions consist of fly ash, soot, and metal and metal oxide fumes. Total particulate emissions have been estimated to be 25 kg/metric ton (50 lbs/short ton) (SH-106). Particulate control equipment usually includes settling chambers, baghouses, and possibly electrostatic precipitators and wet scrubbers.

Wastewater will result from furnace cooling, ingot casting, slag quenching operations, and possibly scrubber blowdown. Discharge rates can be minimized by recycling this water.

Converter Smelting--

The black copper from blast furnace/reverberatory smelting can be further refined to increase the copper content from 70-80 percent to 90-99 percent. Most of the product, called blister copper, is poured and cast or transferred molten to a fire refining furnace. A lesser amount of direct product is produced in the form of copper shot by water quenching.

The process steps involved in converter smelting are a) charging with molten black copper, b) blowing with air to oxidize copper sulfides and other metals, c) deslagging, d) secondary blowing, and e) final slag skimming. Most of the reactions are exothermic; thus, no external heat is required. In fact, if the iron content of the black copper feed is too high, pure copper scrap may have to be added to the charge to help keep the temperature under control. A flux containing silica (*e.g*, sand or glass) is usually added to react with iron oxides. This forms an iron silicate phase which is removed as slag.

Black copper of 70 to 80 percent purity, air, and silica flux are the feed materials. The impurities in the black copper may be iron or copper sulfides, and various other metals and metal oxides such as tin, lead, antimony and zinc.

Wastewater from ingot cooling and slag quenching is also generated. Typical effluent water quality data for a metal cooling operation is given in Table 44.

Electric Crucible Smelting--

Feed containing low copper values can also be refined by using electric heating and pure oxygen in place of air for oxidation. Feed can be either pretreated scrap, raw scrap or black copper from blast furnace/reverberatory smelting. The same sequence of charging, melting, blowing and skimming which is used in the previous two processes is also used here. An advantage of electric heating is the fact that it gives better control over the exothermic portions of the process. Liquid wastes will be similar to the analogous coke-fueled process.

Fire Refining--

In this process, blister copper is further refined to the 99.9 percent purity level. Clean, high grade copper scrap can also be charged directly to this process, which is very similar to the refining process used in the primary copper refining industry. In the fire refining process, copper may be either partially refined to a grade suitable for electrolytic purification or further refined to the practical limit in order to achieve a commercially salable product.

Fire refining can be accomplished in either a reverberatory or a cylindrical tilting furnace. The latter type is generally used with molten copper feed to cast anodes for electrolytic refining. The production of ingot and bar or the melting of blister copper ingots is usually done in a reverberatory furnace.

Both oxidation and reduction of impurities are done in this process. The process steps are a) charging the furnace; b) melting in an oxidizing atmosphere; c) skimming the slag; d) blowing with air or oxygen until the melt is about 10 percent Cu_2O (1 percent total oxygen); e) adding a reducing agent and surface cover of charcoal or coke; f) reducing the oxygen content to 0.03 to 0.05 percent by forcing green maple or birch logs beneath the surface of the melt, agitating the melt with reducing gases such as hydrogen, hydrocarbons, and carbon monoxide that are formed during the "poling" process; g) reskimming the slag, and h) casting the melt into ingots, wire bars, and other products. Reformed gas is commonly used as a reducing agent instead of wooden poles.

Fluxes may be added to extract impurities, *e.g.*, sodium carbonate for arsenic and antimony. A variety of specialized reagents and procedures are available for copper material of special composition (SP-058).

The usual liquid wastes for cooling and quenching operations are produced.

TABLE 44. CHARACTER OF WASTEWATER FROM MOLTEN METAL COOLING AND QUENCHING

	Plant 26 - Gross Loading				Plant 38 - Net Loading				Plant 43 - Gross Loading			
	Intake	Discharge			Intake	Discharge[a]			Intake	Discharge		
			Loading				Loading				Loading	
	Conc., mg/l	Conc., mg/l	kg/MT	(lb/ton)	Conc., mg/l	Conc., mg/l	kg/MT	(lb/ton)	Conc., mg/l	Conc., mg/l	kg/MT	(lb/ton)
Product		Alloy				Alloy				Alloy		
MT/day		27.2				9.7				61.9		
(ton/day)		(30)				(10.7)				(68.2)		
Flow												
l/day	755,000	605,600			29,500	18,200				75,700		
(gal/day)	(199,500)	(160,000)			(7,800)	(4,800)				(20,000)		
Constituent												
Alkalinity	--	104	2.316	(4.632)	79	56.67	NLC[b]		--	448.8	0.549	(1,098)
COD					--	25.0	0.047[c]	(0.094)		--		
Solids Total	160	275.5	1.687[d]	(3.374)	306	207.3	NLC		--	1160	1.419	(2.838)
Solids, Diss.					301	192.63	NLC		—	1020	1.247	(2.494)
Solids, Susp.					5	14.67	0.012	(0.024)	--	140	0.171	(0.342)
TOC					--	9.33	0.018[c]	(0.036)				
Phosphorus	--	0.29	0.006	(0.012)	0.01	0.183	0.0003	(0.0006)				
Cyanide	--	NF[f]	--		0.06	0.057	NLC					
Antimony	--	NF	--		<0.01	0.01	0.0002	(0.0004)				
Arsenic	--	NF	--		<0.02	<0.02	NLC					
Boron	--	NF			0.002	0.047	0.0001	(0.0002)	--	0.0833	0.0001	(0.0002)
Cadmium	--	NF	--		0.05	<0.05	NLC		--	0	NLC	
Chromium	--	0.02	0.0004[d]	(0.0008)					--	0.066	0.0001	(0.0002)
Copper	0.000003	0.560	0.010[d]	(0.02)	0.60	1.067	0.0001	(0.0002)	--	3.376	0.004	(0.008)
Iron	0	0.89	0.020[d]	(0.040)	0.21	0.633	0.0006	(0.0012)	--	1.792	0.002	(0.004)
Lead	--	1.50	0.034	(0.068)	0.11	0.5	0.0006	(0.0012)	--	4.337	0.0053	(0.0106)
Manganese	--	NF	--		0.20	0.133	NLC					
Mercury	--	NF	--		<.001	<.001	NLC					
Nickel	--	NF	--		<0.1	0.1	0.0002	(0.0004)	--	0.164	0.0002	(0.0004)
Zinc	--	0.30	0.007	(0.014)	<0.1	0.4	0.0007	(0.0004)	--	17.834	0.022	(0.044)
Oil and grease	--	8.5	0.189	(0.378)	--	22.33	0.042[c]	(0.084)				
pH		8.5			7.2	7.87				8.9		

[a] Includes some equipment cooling in discharge.

[b] NLC = no loading calculable.

[c] Gross loading.

[d] Net loading.

[e] Casting time estimated at 4 hours.

[f] NF = not found.

Source: EM-378

Electrolytic Refining--

Copper anodes of 99.9+ percent purity may be produced as the output of the fire refining process. Oxygen is the major impurity in the product, usually at the 0.03 to 0.05 percent level. As the anodes dissolve in the electrolysis process, impurities either dissolve in the electrolyte or fall to the bottom of the containing cell to be collected as slime. The cathodes produced are melted and cast in subsequent processes.

The electrolyte accumulates both soluble anode impurities (antimony, bismuth, lead, nickel, iron and zinc) and copper. A replacement rate of up to 75 percent a month of the electrolyte is circulated to liberator cells with insoluble lead anodes and copper starter sheets as cathodes. The copper produced is recycled to the appropriate process, depending on its purity.

The effluent liquids may be concentrated and processed for further metal recovery, *e.g.*, nickel as nickel sulfate. The slime from both the primary electrolysis and the electrolyte purification step is filtered or centrifuged. This material may either be processed further for precious metal recovery or discarded. Much or all of the wastewater may be treated and recirculated. One available analysis of electrolytic process wastewater is given in Table 45.

Electrolytic Winning--

Copper is recovered as impure cathodes from a copper sulfate solution which usually comes from the sulfuric acid leaching process. The copper produced must be further treated electrolytically to attain the purity of regular electrolytic copper.

In this process, the spent electrolyte is continuously bled from the system, regenerated, and recycled. The process steps are a) preparing the electrolyte, b) electrolyzing copper or starter sheet cathodes, c) removing the cathodes, d) cleaning the cathodes, e) replacing the starter strips, and f) regenerating the electrolyte (NA-182).

There will be spent electrolyte residues similar to those of electrolytic refining. There will also be slimes formed from other metals. The amount of slimes formed will depend on the type of scrap originally leached with sulfuric acid (NA-182).

Electrolytic Powder Production--

Pure copper powder is produced by electrolysis from the copper cathodes by electrolytic refining. The process steps are a) use pure electrolytic copper as anodes, b) deposit copper powder, c) filter the powder from the cell electrolyte, d) recycle the electrolyte, e) rinse the powder, f) dry the powder in a reducing atmosphere of hydrogen and carbon monoxide, and g) classify, blend and package the powder. Electricity is required as the driving force for the electrolytic reaction, and heat is required to dry the powder.

TABLE 45. CHARACTER OF WASTEWATER FROM ELECTROLYTIC REFINING (TREATED BEFORE DISCHARGE[a])

Volume:	94,600 ℓ/day (25,000 gal/day)
Operation:	Electrolytic refining
Production:	179 MT/day (197 short tons/day)[b]

Constituent	Intake mg/ℓ	Discharge, mg/ℓ	Net Conc. mg/ℓ	Net Loading kg/MT	Net Loading (lb/ton)
Alkalinity	22	27	5	0.0026	(0.0052)
BOD, 5-day	16	0	16	NLC[c]	
COD	29	--	--	NLC	
Solids	30	1776	1746	0.922	(1.844)
Diss. Solids	40	1611	1571	0.830	(1.661)
Susp. Solids	3	12	9	0.0048	(0.0096)
Total Vol. Solids	-	336	336	0.178	(0.356)
Nitrate (as N)		0.22	0.22	0.00013	(0.00026)
Sulfate (as S)		1047	1047	0.555	(1.110)
Sulfite (as SO)		12	0.2	0.00017	(0.00035)
Chloride	8.0	4.1	-3.9	NLC	
Aluminum	4	0	-.4	NLC	
Antimony		0.0005	0.0005	2.6x10^{-7}	(5.2x10^{-7})
Arsenic		0.0	0	NLC	
Cadmium		0.0	0	NLC	
Calcium		94	94	0.0498	(0.0996)
Chromium		0.00003	0.00003	2x10^{-8}	(3x10^{-8})
Copper		0.00006	0.00006	3x10^{-8}	(6x10^{-8})
Iron		0.0047	0.0047	2.6x10^{-6}	(5.2x10^{-6})
Lead		0.0004	0.0004	1.7x10^{-7}	(3.5x10^{-7})
Magnesium		0.0014	0.0014	8.7x10^{-7}	(1.7x10^{-6})
Manganese		0.0027	0.0027	1.3x10^{-2}	(2.6x10^{-6})
Mercury		0		NLC	
Nickel		0.00037	0.00037	1.7x10^{-7}	(3.4x10^{-7})
Potassium		7.2	7.2	0.0039	(0.0079)
Silver		0.00001	0.00001	5x10^{-9}	(1x10^{-8})
Sodium		3.1	3.1	0.0018	(0.0035)
Zinc		0.00065	0.00065	3x10^{-7}	(6x10^{-7})
Oil and Grease	6.4				
pH	7.6	8.0			
Temp (Win), C(F)	14 (57)	27 (80)			
Temp (Sum), C(F)	22 (72)	29 (85)			

[a] Discharge would be outflow of excess washdown water from treatment plants in event of breakdown and is not continuous.

[b] Production at time of permit application (1971).

[c] NLC = no loadings calculable.

Source: EN-378

Atmospheric emissions include gaseous emissions of carbon monoxide, hydrogen, and possibly arsine and unburned fuel, and particulate emissions consisting of dusts from the drying and powder hauling steps. No quantitative data are available.

Liquid wastes similar to the spent electrolyte solutions generated by electrolytic refining are produced.

SECONDARY LEAD/ANTIMONY INDUSTRY

Industry Description - Secondary Lead/Antimony

The secondary lead and antimony industries are grouped together for the purposes of this assessment because a considerable overlap exists between the population of companies producing secondary lead and antimony products and those using similar raw materials. The major differences between these industries are a) some antimony is recovered from antimony-bearing scrap that does not contain lead and b) the use of shaft and rotary furnace smelting in recovering antimony.

The lead/antimony segment of the secondary nonferrous metal industry recovers, processes, remelts, refines, and alloys lead- and antimony-bearing scrap to produce lead, lead-antimony alloys, and lead oxides. According to the Commodity Data Summaries 1976, the secondary lead/antimony segment consisted of 130 individual plants (US-357). Sixty-eight of these plants were identified in a more recent report (CO-R-720). These plants are mainly located in or near the following cities: New York, Philadelphia, Baltimore, Cleveland, Chicago, Baton Rouge, Dallas, Los Angeles, and San Francisco.

The total 1975 domestic recovery of secondary lead excluding that recovered at primary plants was 520,000 metric tons (563,000 short tons) valued at 260 million dollars (US-357). Old lead-bearing scrap accounted for 86 percent of the total secondary recovery of lead metal and alloys. Old and new scrap accounted for approximately 48 percent of the total domestic production and 47 percent of the total consumption. Storage batteries accounted for 57 percent of this scrap (US-357). The consumption of lead metal and alloys was by 600 firms in virtually all states (US-357). The major end use of lead was for transportation, 53 percent as batteries and 16 percent as gasoline additives (US-357). Other major end-uses of lead and alloys included: a) electrical materials, b) ammunition, c) paints, and d) construction.

The total 1975 production of secondary antimony was 15,100 metric tons (16,600 short tons) valued at 58.1 million dollars (US-357). Approximately 55 percent of the 1975 domestic consumption of antimony was derived from scrap. The major uses of antimony were:

- Storage batteries (44%)
- Chemicals (17%)
- Fire retardants (15%)
- Rubber products (10%)
- Ceramic and glass (6%)

The major types of scrap processed by this segment are (NA-182):

- Soft lead
- Hard lead
- Cable lead
- Battery-lead plates
- Mixed common babbitts
- Solder and tinny lead
- Type metals
- Drosses and residues
- Antimony-bearing metal

The scrap breakdown used in producing antimony for 1975 was (US-357):

- Battery plates (65%)
- Type metal (14%)
- Antimony-bearing metal (21%)

The production of old scrap processed by this segment is relatively high in comparison to scrap sources for other major segments. Battery scrap is the major old scrap source; all other types of old scrap are from a variety of domestic sources. The scrap contains elemental lead, compounds of lead, or lead alloyed with tin, antimony, arsenic, cadmium, copper, indium, silver, zinc, tellurium, or bismuth. The scrap can also contain organic contaminants such as insulation, grease, and oil as well as sulfur compounds. Products from the lead/antimony segment of the secondary nonferrous metal industry are (NA-182):

- Soft lead ingots
- Semisoft lead ingots
- Hard lead ingots
- Lead alloy ingots
- Battery lead oxide
- Lead pigments (Pb_3O_4 and PbO)

Soft lead is a high-purity lead. These are generally products of pot furnace refining.

Semisoft lead usually is produced in a reverberatory furnace and contains 0.3 to 0.4 percent antimony and up to 0.05 percent copper (DA-069). Hard lead is normally a blast furnace product. A typical composition includes 5 to 12 percent antimony, 0.2 to 0.6 percent arsenic, 0.5 to 1.2 percent tin, 0.05 to 0.15 percent copper, and 0.001 to 0.01 percent nickel (DA-069).

Wastewater Source Identification - Secondary Lead/Antimony

Lead and antimony are recovered from scrap by three major manufacturing operations: 1) scrap pretreatment, 2) smelting, and 3) refining/casting. The scrap pretreatment operation involves physical crushing and separating as well as sweating in a rotary or reverberatory furnace. The smelting operations for lead take place either in a reverberatory furnace which generally produces a semisoft lead, or in a blast furnace, which produces a hard lead. Antimony smelting operations include shaft, rotary, reverberatory, and blast furnace smelting. The refining/casting operation involves fluxing partially refined lead in a pot kettle to produce a soft lead which can be cast as a product or alloyed, or oxidizing lead products to produce battery lead oxides or lead oxide pigments.

Five of the sixteen processes in the secondary lead/antimony industry are potential sources of water pollution. These five processes are: a) battery breaking, b) zinc leaching, c) shaft furnace smelting, d) reverberatory furnace smelting, and e) blast furnace smelting. The water pollution from the latter two processes is from the effluent of wet scrubbers.

Aqueous effluents from the battery breaking process are significant because 57 percent of the total secondary lead production comes from old storage batteries (US-257). Assuming that the old batteries contain only one percent sulfuric acid by weight and the average lead concentration in the scrap batteries is 76 percent (CO-371), the total annual sulfuric acid emissions from this process would be approximately 3900 metric tons (4300 short tons). This effluent is hazardous and needs to be controlled. The other constituents in these aqueous effluents consist of dissolved lead, lead compounds, and metal alloys.

The zinc leaching process is another major source of water pollution in this industry. The constituents in the wastewater consist primarily of the spent leaching liquor, sulfuric acid, zinc. antimony, lead, copper, metal sulfides, and metal chlorides. The effluent from this process is usually neutralized and sent to unlined settling ponds.

The wet scrubber effluent from the reverberatory and blast furnace smelting processes contains hazardous constituents found in the processes' air emissions. These aqueous effluents are usually sent to unlined settling ponds.

Table 46 lists each of the processes for which effluent streams have been identified and summarizes the available data on the characteristics of these wastewaters. The following discussion describes the process specific sources of these wastewaters in more detail.

Battery Breaking--

Fifty-seven percent of secondary lead and 65 percent of secondary antimony comes from obsolete automobile batteries. This process separates the lead from nonmetallic portions of the battery by a) draining, b) crushing

TABLE 46. SUMMARY OF POLLUTANTS IN INDUSTRIAL WASTEWATER SOURCES - SECONDARY LEAD

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)	Ref.	Comments
Secondary Lead Industry				
Battery Breaking				
- Battery acid		Concentrated H_2SO_4 containing Pb compounds and other alloying compounds.		
Zinc Leaching				
- Spent leaching solution		Dilute sulfuric acid containing: Zn Sb Pb Cu Chlorides Sulfides	EN-399	Neutralized and discharged to settling ponds.
Shaft Furnace Smelting				
Rotary Furnace Smelting				
Reverberatory Furnace Smelting				
Blast Furnace Smelting				
Reverberatory Smelting				
Blast (Cupola) Furnace Smelting				

the battery, and c) manually screening to separate the lead protion from nonmetallic portions (NA-182). The separated scrap normally has the following composition (CO-371):

- $PbSO_4$, 30-40%
- PbO_2, 15-20%
- PbO, 2-3%
- Nonmetallic content, 4-6%
- Pure and antimonial lead, balance

The battery scrap fed to the process is composed mainly of the following constituents:

- pure and antimonial lead from plate grids, connections, bridges, and terminal posts;
- copper from terminals;
- lead oxides (PbO and PbO_2) and lead sulfate ($PbSO_4$) pastes;
- separators and outercase residues of ebony, glass fiber, paper, polyvinyl chloride, and polystyrene (CO-371).

Waste products are primarily solid, with lesser amounts of liquid and dusts. Solid wastes include the organic materials used in battery case construction contaminated with residual sulfuric acid and lead compounds. Liquid wastes are composed of sulfuric acid, water and lead and alloying compounds.

Zinc Leaching--

In this process, zinc is leached from the collected particulate matter that is emitted from the Reverberatory Smelting Process. The particulate matter is washed with a stream of dilute sulfuric acid to dissolve the zinc and the undissolved residue is fed to the blast furnace.

Baghouse residues contain tin, antimony, copper, zinc, lead, sulfides, and chlorides and dilute sulfuric acid. Typical concentrations of zinc and lead are 13 to 18 percent by weight, respectively.

The aqueous effluent consists of dilute sulfuric acid containing zinc compounds and traces of antimony, lead, copper, sulfides, and chlorides. The spent leaching liquor is neutralized and discharged to settling ponds (EN-399).

Shaft Furnace Smelting--

A shaft furnace containing layers of coke is used to melt paste constituents resulting from battery breaking or rotary furnace smelting (mostly sulfates and oxides of lead). The salts are thereby reduced to lead metal of high purity. Lime may be added to counter the drossing effects of silicates present. Lead sulfate, lead oxides, coke (reducing agent), and lime are inputs for this process.

Potential effluents from this process are water jacket or mold cooling water or blowdown from wet scrubbers.

Rotary Furnace Smelting--

Scrap metal and a salt mixture consisting of a paste of metal oxides and sulfates are introduced into a rotary furnace in which the temperature is controlled to effect melting of the metal, but not of the salt mixture. The specific gravity difference between lead and the metal salts causes the salts to float, which makes possible the separation of the alloyed metal containing 4 to 6 percent antimony (CO-371). The salts are removed and further processed in a shaft furnace. The rotary furnace is heated to temperatures of 600 to 700°C (CO-371).

Potential effluents from this process are mold cooling water and blowdown from wet scrubbers.

Blast Furnace Smelting--

Slag from the reverberatory furnaces, babbitt metal, type metal and battery scrap are charged to a blast furnace to produce a lead-antimony alloy. A mixture of these metal scraps, slags, and coke is continuously charged to the furnace where it is heated to form the molten alloy and waste slag. The oxides of antimony and lead contained in the slag from the reverberatory furnace are reduced to the metallic state by the carbon monoxide formed by combustion of coke in the furnace. This process is very similar to Blast Furnace Smelting in the Secondary Lead Smelting segment. Waste cooling water from the furnace water jacket constitutes a liquid waste stream.

Reverberatory Smelting--

This process is used to partially purify and densify lead scrap. The furnace feed can be pretreated, untreated, or mixed scrap. Pretreated lead scrap, battery plates, oxides, drosses, lead residues, and collected flue dusts are all inputs for this process. The process steps are: a) continuously charging the furnace with a mixture of lead scrap and collected flue dusts as the charge melts, b) periodically tapping the antimonial slag that rises to the surface of the melt, and c) tapping the molten lead which may be fed to a refining/casting process or cast into ingots as a semisoft or possibly hard lead product (NA-182, SI-106). The slag is fed to a blast furnace.

The temperature in the reverberatory furnace is high enough to oxidize the sulfides present in the lead scrap to sulfur dioxide and trioxide, which are emitted in the stack gases along with normal combustion products. Particulate emission concentrations range from 16 to 50 g/m^3 (7 to 22 grains/

ft^3) and includes oxides, sulfides, and sulfates of lead, tin, arsenic, copper, and antimony (EN-071). The particle size of unagglomerated particulate matter ranges from 0.07 to 0.4 microns, with a mean diameter of 0.3 microns (DA-069). Typical constituents of collected particulate matter include tin, antimony, copper, lead, zinc, sulfides, and chlorides. The lead content is typically about 17 to 18 percent (EN-399).

Particulate emissions are generally controlled with a gas settling/cooling chamber and a fabric filter. Control efficiencies in excess of 99 percent can be effected by this system. Wet scrubbers are sometimes employed to control sulfur oxide emissions (NA-182, EN-071). A potential wastewater stream is wet scrubber effluent.

Blast (Cupola) Furnace Smelting--

This process utilizes pretreated scrap, antimonial (reverberatory) slag, and rerun (recycled) slag to produce a hard lead as a final or intermediate product. The blast or cupola furnace is used to perform this function. The blast furnace is a refractory-lined cylinder open at the top into which alternate layers of metal, coke, and flux are charged. The process steps are: a) adding the charge intermittently as melting proceeds, b) introducing air through the tuyeres in the bottom to permit combustion of the coke in the charge (this reaction provides both heat and a reducing atmosphere), c) removing the molten lead continuosly, d) removing slag intermittently, and e) casting the molten hard lead into large ingots or transferring to refining kettles. Approximately 70 percent of the lead charged can be recovered as product. The remaining 30 percent is rerun slag.

A typical charge to the blast furnace contains: 82.5 percent drosses, oxides, leaching residue, and reverberatory slag; 5.5 percent coke; 4.5 percent rerun slag; 4.5 percent scrap iron; and 3 percent limestone (DA-069). The drosses consist of copper, caustic, and dry drosses from kettle furnace refining/casting processes. The reverberatory slag is composed of lead, silica, tin, arsenic, copper, and antimony. The rerun slag is a highly silicated slag tapped from previous blast furnace runs. The iron and limestone form an oxidation-retardant flux that floats to the top of the melt.

Waste streams produced by this process include atmospheric emissions, solid wastes, and in some cases, wet scrubber effluent. Gaseous emissions can be controlled by afterburners or wet scrubbers. Baghouses with precoolers have generally been the most acceptable particulate control devices. The efficiency of particulate removal by baghouses generally exceeds 95 percent. A potential wastewater stream is wet scrubber effluent.

SECONDARY ZINC INDUSTRY

Industry Description - Secondary Zinc

The secondary zinc industry processes zinc-bearing scrap to produce metallic zinc and zinc-base alloys. The processes used in this segment of the nonferrous metal industry include mechanical, hydrometallurgical, and pyrometallurgical scrap pretreatment techniques, remelting and distilling, scrap zinc oxide reduction to metallic zinc, and zinc oxide production through modification of distillation operations.

The zinc segment of the secondary nonferrous metal industry consists of only twenty-three firms (CO-R-720). Three primary smelters and six secondary smelters accounted for the total secondary zinc slab produced, 44,000 metric tons (49,000 short tons), in 1975.

The raw materials used by the secondary zinc industry are zinc- and copper-based scrap, fluxes, alloying agents, and individual process inputs such as sodium carbonate, water, and carbon.

Classes of new scrap consumed by smelters and distillers include new clippings, skimmings and ashes, die-cast skimmings, galvanizers' dross, flue dust, and chemical residues. Approximately three-fourths of all new scrap processed is zinc- and copper-base alloys from galvanizing and die-casting pots (MC-194). Included in the old scrap category are old zinc engravers' plates, diecastings, and rod and die scrap. The total amount of zinc scrap consumed by smelters and distillers in 1975 amounted to 263,000 metric tons (290,000 short tons) (US-357).

The zinc content of scrap may range from 40 to 100 percent. Typical die-cast scrap composition may include 3 to 5 percent aluminum and 1 to 3 percent copper, although magnesium is now frequently used in place of copper (MO-170). The main sources of zinc scrap are listed below (CA-305, MC-200):

- brass mills
- galvanizing plants
- chemical plants
- engraving platemakers
- fabricators of products from roller zinc
- die casters
- auto wrecking yards
- electric utilities
- railroads
- aircraft plants
- demolition contractors
- government agencies.

Other input materials to the secondary zinc industry are alloying agents. The most common ones are aluminum, copper, lead, and magnesium.

Fluxing agents are used to remove impurities present in scrap. Those most in use include zinc chloride and ammonium chloride although the latter causes fuming and is not employed except for special cases. Secondary zinc is recovered as zinc slabs, zinc dust, and zinc oxide. Zinc slabs can either be the pure metal or zinc alloys.

Wastewater Source Identification - Secondary Zinc

Three general classes of operations are carried out in the secondary zinc industry: scrap pretreatment, melting, and refining.

The purpose of scrap pretreatment is to partially remove both metal and nonmetal contaminants and to physically prepare the scrap for further processing. The pretreatment processes in use are based on mechanical, pyrometallurgical, or hydrometallurgical methods. Mechanical processing involves physical reduction of the scrap and some means of separating the zinc from contaminating components. Sweating is the term applied to the pyrometallurgical process used to separate zinc from higher melting metal and inorganic impurities. Kettle, rotary, reverberatory, muffle, and electric resistance furnaces are employed to sweat zinc-bearing scrap. The primary hydrometallurgical pretreatment method is sodium carbonate leaching which is used to process skimmings and residues.

In the melting operation, scrap is melted and usually fluxed to remove impurities in crucible, kettle, reverberatory, or electric induction furnaces. The product of this step serves as feed to the refining operation.

Secondary refining is based on distillation of metallic zinc and in some cases subsequent oxidation. This type of refining removes the metallic and nonmetallic contaminants remaining after pretreatment and melting. Some secondary plants carry out reduction processes to recover zinc from dross, air pollution control residuals, or contaminated zinc oxide.

While only one process is directly associated with a wastewater stream (Sodium Carbonate Leaching), cooling water used in the casting step is another potential liquid effluent source. Wastewater from the leaching process is treated by precipitation. Metal cooling water is either sent to settling ponds or to the sewer.

Solid wastes from this process include skimmings, drosses and unmelted residues from the sweating and melting operations; distillation residues which contain 10 to 50 percent zinc; and baghouse dusts. Depending on their metal content and the plant's processing scheme, these solids may be recycled. Residues which are not recycled are typically disposed of in open landfill sites. Runoff and leachate from these disposal areas represent potential hazards to surface- and ground-water reservoirs because of the hazardous constituents contained in these solid wastes.

Table 47 lists each of the processes for which effluent streams have been identified and summarizes the available data on the characteristics of these wastewaters. The following discussion describes the sources of these wastewaters in more detail.

TABLE 47. SUMMARY OF POLLUTANTS IN INDUSTRIAL WASTEWATER SOURCES - SECONDARY ZINC

Source	Flow (ℓ/min)	Stream Composition (mg/ℓ)	Ref.	Comments
Secondary Zinc Industry				
Sodium Carbonate Leaching				
- Spent leaching solution	No data.	No data.	CO-R-467	Consists primarily of $NaCl$ and Na_2CO_3.
Kettle (Pot) Melting Crucible Melting Reverberatory Melting Electric Induction Melting				
- Mold cooling water	No data.	No data.	CO-R-467	Only in cases where water cooling is used.

Sodium Carbonate Leaching--

Residues are chemically treated to leach out and convert zinc to the oxide form. The scrap is first crushed and washed. In this step, the zinc is leached out of the material. The aqueous stream is treated with sodium carbonate (Na_2CO_3), causing zinc to preciptiate as the hydroxide and/or carbonate. The precipitate is then dried and calcined yielding crude ZnO. The output from this process is normally sent to a primary smelter for reduction to elemental zinc. Aqueous effluents from this process contain sodium chloride, excess sodium carbonate, and various soluble compounds not precipitated by sodium carbonate.

Kettle (Pot) Melting--

In zinc scrap melting processes, zinc is separated from nonmetallic residues and metal attachments having higher melting points, usually with fluxing. The following steps are involved in kettle melting: a) charging of scrap to the furnace, b) melting the zinc fraction, c) fluxing, d) agitating to effect separation of the dross, e) skimming, and f) pouring into ladles or molds. The output from this process can be sent directly to a distillation furnace or alloying process unit, or cast into blocks before further processing. In cases where mold cooling water is used, this would constitute a liquid waste source.

Crucible Melting--

Melting can also be carried out in crucible furnaces (DA-069). Refer to the description of the process steps involved under Kettle (Pot) Melting. Sweated zinc scrap and flux are input materials for this process. Mold cooling constitutes a potential source of wastewater from this process as in the Kettle Melting process.

Reverberatory Melting--

Zinc melting may also be carried out in reverberatory furnaces. The charge may be either the product of a reverberatory sweating operation or other pretreated scrap. Refer to Kettle (Pot) Melting for a description of the process steps involved. Mold cooling water is a potential source of wastewater from this process.

Electric Induction Melting--

Electric induction furnaces are also used to melt zinc scrap. In this process a molten heel must be left in the furnace at the start of each heating cycle. See Kettle (Pot) Melting for a description of the process steps. The output from this process is sent to a refining process. Mold cooling water is the only potential source of wastewater from this process.

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APPENDIX A

SUMMARY OF POLLUTANTS IN INDUSTRIAL WASTEWATER SOURCES

The following table contains the data concerning industrial wastewater containing metals which were found during this study. It is not a comprehensive list of all available data. Rather, it is intended to provide a general reference for the quantity and type of pollutants present in each wastewater stream.

TABLE A-1. SUMMARY OF POLLUTANTS IN INDUSTRIAL WASTEWATER SOURCES

Source	Stream Composition (mg/ℓ)	Reference	Comments
1. Cement Industry			
Cooling Tower Blowdown	Cr-P	EN-148	
Process Operations	Pb-P	EN-148	From oyster shells
	Fe-P	DE-170	
	Al-P	DE-170	
2. Electronics Industry			
Batteries			This industry is largest consumer of Pb. Lead losses range from 4.54-6810 mg per battery manufactured. Water usage was 11-77 gal/battery.
- dry cell battery manuf.	Mn-P	PA-322	
- plate forming	Pb particulate, 5-48	PA-322	Low pH stream (1.3-2.6)
	Pb dissolved, 0.4-66.5	PA-322	
Electrical Equipment Prod.	Hg-P	PA-322	Second largest user of Hg.
Television Tube Manuf.	Pb, 400	RO-385 PA-322	
3. Explosives Industry			
Ammunition Plant	Pb, 6.5	PA-322	
Lead Azide and Lead Styphnate	Pb, 0-200	EN-439	
Match and Fireworks Prod.	Mn-P	PA-322	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
4. Glass and Ceramics Industry			
Glass Manuf.	As-P	PA-322	
	Mn-P	PA-322	
	Cd-P	PA-322	
	Cr-P	DE-170	
	Zn-P	DE-170	
5. Inorganic Chemicals Industry			
Boric Acid Production	As, .036 kg/Mg	VE-065	
Caustic Evaporation and Salt Recovery	Pb, 0-.22 kg/Mg	VE-065	Pb from corrosion of anode
Chloralkali Industry	Hg dissolved, .080-2.8	PA-322	.05-.25 kg/Mg
	Hg suspended, 14.0 mg/kg	PA-322	
- brine sludge	Hg, 150-1500	PE-222	1.4 m tons/day
• brine clarifier • brine filter • salt saturator residue			
- wastewater from:	Hg, 0.3-18	PE-222	110-190 ℓ/min
• floor washing • purge streams from cell end-box wash water recycle • purge from brine system • drainage from filtration area • tank cleaning			

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
5. Inorganic Chemicals Industry (Cont'd)			
Chrome Yellow Production	Cr, 5.7-7 kg/Mg Pb, 0-2.1 kg/Mg	VE-065	
Chromic Acid Production	Cr, 0.5-1.0 kg/Mg	VE-065	
Chromic Oxide Production	Cr, 3-95 kg/Mg	VE-065	
Cooling Tower Blowdown	Cr, 0-1300	MA-760	
Cooling Tower Blowdown	Cr, 0-250 Zn, 0-30	EN-145	
Cooling Tower Blowdown	Cr, 10-60	CH-A-386	
Fertilizers	Cu-P	PA-322	
	Fe-P	PA-322	
- fertilizer mill	Hg, .00026-.004	PA-322	
- phosphate fertilizer production	As-P	EN-145	
	Cd-P	EN-145	
- specialized fertilizer production	Mn-P	PA-322	
Molybdatechrome Orange Prod.	Cr, 0.6 kg/Mg Pb, 0.7 kg/Mg	VE-065	
PCl_3 Production	As-P	EN-150	
Pesticides	As-P	PA-322	
	Hg-P	PA-322	
- production of Paris Green and calcium meta-arsenate	As (as As_2O_3), 362	PA-322	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
5. Inorganic Chemicals Industry (Cont'd)			
Phosphoric Acid Production	As-P	VE-065	
	Cd-P		
Production of Pigments using Cadmium Sulfide or Cadmium Selenide	Cd, 2-120 g/day (8 g/day avg)	PA-322	
Sodium Bisulfite Production	Cu, 0.1-0.5	VE-065	
	Cr, 0.1-0.5	VE-065	
	Pb, 0.15-0.5	VE-065	
	Fe, 40-250	VE-065	
Sodium Nitrate Production	Fe, 0.5	VE-065	
	Cu, 1.0	VE-065	
	Cr, 0.3	VE-065	
	Pb, 0.7	VE-065	
Sulfuric Acid Production	As, 200-500	PA-322	
Titanium Oxide Production	Ti, 17 kg/Mg	VE-065	Lime treatment
	Fe-P	PA-322	
Titanium Tetrachloride Production	Ti, 50 kg/Mg	VE-065	Lime treatment
	Cr, 4 kg/Mg	VE-065	
	Fe, 2-380 kg/Mg	VE-065	
	V, 2-6 kg/Mg	VE-065	
	Al, 4-24 kg/Mg	VE-065	
	Cu, 62 kg/Mg	VE-065	
Zinc Oxide Production	As, 0.05 kg/Mg	VE-065	
	Zn, 0.07 kg/Mg	VE-065	
	Pb, 0.09 kg/Mg	VE-065	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
5. Inorganic Chemicals Industry (Cont'd)			
Zinc Yellow Production	Cr, 12 kg/Mg Zn, 19.5 kg/Mg	VE-065	
6. Leather Tanning and Finishing Industry			
Dye Rinse	Cr, 51	EN-156	
Dye Rinse	Cr, 40	CH-A-386	
Process Operations	As-P Fe-P Cr(VI), 40	PA-322 PA-322 PA-322	
7. Metal Fabrication and Finishing Industry			
Appliance Manuf.	Fe, .09-60 Cu, 0-11	PA-322 PA-322	
Automobile Assembly	Fe, 3-4	PA-322	
Automobile Heating Control Mfg.	Cd, 14-22	PA-322	
Brass and Copper Wire Mill	Cu, 4.4-880	PA-322	
Pickling Wastes	Cu, 0.4-22 Ni, 3	PA-322 PA-322	
Plating Bath Dumps	Pb, 140 Zn, 5,000-34,000 Cd, 2,000-23,000 Cr(VI), 10,000-50,000 Cr(VI), 200-75,000 Cr(VI), 10,000-270,000 Ag, 13,000-45,000	PA-322 PA-322 PA-322 CH-A-386 PA-322 PA-322 PA-322	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
7. Metal Fabrication and Finishing Industry			
Plating Drag Out	Pb, 0-2	PA-322	
	Zn, 0-220	PA-322	
	Ni, 0-900	PA-322	
	Cu, 0-900	PA-322	
	Cr(VI), 1-100	PA-322	
	Cd, 7-240	PA-322	
	Ag, 50-250	PA-322	
	Fe, 0-60	PA-322	
8. Mining Industry			
Acid Mine Drainage	Ni, 0.46-3.4	PA-322	
Acid Mine Drainage (Abandoned Mines)	As, 0-22.3	PU-A-020	Untreated
	Cd, .02-1.0	PU-A-020	
	Cu, .2-128.0	PU-A-020	
	Fe, 20-800	PU-A-020	
	Pb, 0-3.0	PU-A-020	
	Mn, 4.5-14.0	PU-A-020	
	Ni, .03-.5	PU-A-020	
	Al, .1-82.5	PU-A-020	
	Zn, 6.8-294.0	PU-A-020	
Bauxite Ore - Raw Mine Drainage from Open Pit Mine	Al, 5.9-8.8	EN-394	
	Zn, .36-25.3	EN-394	
Coal - Mine Wastewater	Zn, .01-12.7	EN-377	
	Ni, .01-5.6	EN-377	
	Al, .01-271	EN-377	
	Mn, .01-127	EN-377	
	Fe, 40-330	PA-322	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
8. Mining Industry (Cont'd)			
Copper Ores - Discharge Mill Wastewater	Pb, .1-2.0	EN-394	15M - 101M m^3/d
Copper Ores - Raw Mill Wastewater	Pb, <.1-2.8	EN-394	Settled in tailings pond
	Cu, .08-900	EN-394	
	Ni, .05-2.8	EN-394	
	Zn, .05-8.5	EN-394	
Copper Ores - Raw Mine Water	Cu, 0.5-92	EN-394	
	Fe, 0.1-2,000	EN-394	
	Mn, 0.9-100	EN-394	
	Zn, 0.1-172	EN-394	
Ferroalloy Ores - Raw Mill Wastewater	Cd, .19-.74	EN-394	
	Cu, 21-51	EN-394	
	Mn, 50-56	EN-394	
	Pb, 2.1-9.8	EN-394	
	Zn, 25-76.9	EN-394	
	Mo, 5.3-17.5	EN-394	
	Fe, 1305-1500	EN-394	
Ferroalloy Ores - Tailings Discharge	Fe, 0.44-24	EN-394	
	Mn, 0.19-50	EN-394	
	Mo, 0.5-2.2	EN-394	
	Mo, 2.0-4.0	RA-S-614	
Iron Ores - Mine Discharges	Pb, 0.001-.100	PA-322	Settled in tailings pond
	Hg, 0.002-2.00	PA-322	
	Mn, 0.001-18.0	PA-322	
	Zn, 0.001-8.0	PA-322	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
8. Mining Industry (Cont'd)			
Iron Ore - Raw Mill Wastewater	Fe, 0.20-10.0	EN-394	
	Pb, 0.10-5.0	EN-394	
	Mn, 0.007-20.0	EN-394	
	Zn, 0.006-10.0	EN-394	
Lead/Zinc Ores - Raw Mine Water	Pb, 0.1-4.9	EN-394	Settled in tailings pond
	Zn, .03-38	EN-394	
	Mn, .02-57	EN-394	
	Hg, <.0001-.1	EN-394	
	Cd, 0-1,000	PA-322	
Silver Ore - Raw Mine Wastewater	Fe, .33-2.05	EN-394	
	Mn, .43-6.3	EN-394	
9. Organic Chemicals Industry			
Acetaldehyde Production	Cr, 2.7	EN-153	
Butadiene Production	Fe, 45.1	EN-153	
Dimethyl Terephthalate Production	Zn, 1.11	EN-153	
	Cu, 29.7	EN-153	
	Cr, 3.51	EN-153	
Ethylene/Propylene via Pyrolysis	Zn, 3.2	EN-153	
	Cr, 4.35	EN-153	
Methyl Methacrylate Production	Cu, 288	EN-153	
	Fe, 500	EN-153	
Petrochemicals	Hg-P	PA-322	Cl is usually associated with Ca or Al
	Al-P	DE-170	
	Sn-P	DE-170	
	As-P	DE-170	
	Cd-P	DE-170	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
9. Organic Chemicals Industry (Cont'd)			
Raw Waste Loads for General Organic Chemical Process Operations	Zn, 0.10-3.2	EN-153	
	Cu, 0.10-288	EN-153	
	Fe, 0.40-500	EN-153	
	Cr, 0.04-4.58	EN-153	
Terephthalic Acid Production	Zn, 1.57	EN-153	
	Cu, 24.6	EN-153	
	Fe, 12.7	EN-153	
	Cr, 4.58	EN-153	
Tetraethyl Lead Manuf. (Gasoline Additives)	Pb, 45	PA-322	This represents second largest use of lead
	Pb, inorg. 66.1-84.9	PA-322	
	Pb, org. 126.7-144.8	PA-322	
10. Paint and Ink Industry			
Process Operations	Cr, 0.08	EN-409	Pigments and other reactants
	Pb, 0.4-5.0	EN-409	
	Zn, 2.6-77.4	EN-409	
	Cu, 0.04-0.4	EN-409	
	Fe, 2.5-139	EN-409	
	Al, 29.5	EN-409	
	As-P	PA-322	
	Mn-P	PA-322	
11. Petroleum Refining Industry			
Cooling Tower Blowdown	Cr, 0-6	EN-407	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
11. Petroleum Refining Industry (Cont'd)			
Process Operations	Al-P	EN-407	
	As-P	EN-407	
	Cd-P	EN-407	
	Co-P	EN-407	
	Cu-P	EN-407	
	Fe-P	EN-407	
	Hg-P	EN-407	
	Pb-P	DE-170	
	Ni-P	EN-407	
	V-P	EN-407	
	Zn, .04-1.84	EN-407	
	As-P	PA-322	
	Cu-P	PA-322	
	Fe-P	PA-322	
12. Photographic Industry			
Fixer and Developer Concentrate Effluents	Ag, 450-2,950	LA-A-337	
Wash Water Effluents	Ag, 1.3-5.6	LA-A-337	
	Hg	DE-170	
	Pb	DE-170	
13. Plywood, Hardwood, and Wood Preserving Industry			
Preservatives and Fire Retardants	As-P	EN-382	
	Cr, 0.23-1.5	PA-322	
	Cu-P	EN-382	OH precip.
	Zn-P	EN-382	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
14. Pulp and Paper Industry			
Groundwood Pulp Production	Zn-P	PA-322	
Kraft Process Paper Mill	Cu-P	PA-322	
	Cr-P	DE-170	
	Ni-P	DE-170	
	Sn-P	DE-170	
	Pb-P	DE-170	
Newsprint Paper Production	Zn-P	PA-322	
Paper Mill Effluent	Hg dissolved, .002-.0034	PA-322	
	Hg suspended, 5.6 mg/kg		
Paper Mill Settling Pond	Hg dissolved, .00008	PA-322	Note: Hg formerly used as fungicides, slimicides, biocides
	Hg suspended, 10 mg/kg	PA-322	
15. Steam Generation Industry			
Cooling Tower Blowdown	Cr-P	DE-170	
	Zn-P	DE-170	
Metal Cleaning			
Acid Cleaning	Cu, 400-1,000	SA-S-342	
	Fe, 4,000-10,000	SA-S-342	
Air Preheater Wash	Cu, 0.35-40	SA-S-342	
	Fe, 376-6,000	SA-S-342	
Boiler-Fireside Wash	Cu, 0-5	SA-S-342	
	Fe, 0-300	SA-S-342	

(Continued)

TABLE A-1 (Continued)

Source	Stream Composition (mg/ℓ)	Reference	Comments
16. Steel and Iron Industry			
Chrome Plating	Fe, 30.6-42.9	BR-479	
	Cr, 49-85.4	BR-479	
Cold Finishing	Fe, 60-150	PA-322	
Degassing	Zn, 2.01-7.76	EN-161	
	Pb, 0.47-1.39	EN-161	
	Mn-P	EN-161	
	Cu-P	EN-161	
	Al-P	EN-161	
	Hg-P	EN-161	
Galvanizing	Cr, .56-3.3	BR-479	
	Zn, .31-1.1	BR-479	
	Fe, 4.8-25.5	BR-479	
Open Hearth	Zn, 2.06-880	EN-161	
	Mn-P	EN-161	
	Hg-P	EN-161	
	Cu-P	EN-161	
Pickling	Cu-P	PA-322	
	Ni-P	PA-322	
	Mn-P	PA-322	
	Fe, 60-96,800	PA-322	
- pickle bath rinse	Fe, 60-1,300 (210 avg)	PA-322	
- pickle bath rinse	Fe, 200-5,000	PA-322	
- spent acid pickling solution	Fe, 70,000-96,800	PA-322	Most significant industrial source of soluble iron waste.

(Continued)

TABLE A-1 (Continued)

Sources	Stream Composition (mg/ℓ)	Reference	Comments
16. Steel and Iron Industry (Cont'd)			
Scrap Detinning	Fe, 3.7-14.2 Sn, 9.7-1,440 Cr, 0-.15	BR-479 BR-479 BR-479	
Tin Plating	Fe, 18.3 Cr, 12.6 Sn, 61.4	BR-479 BR-479 BR-479	
17. Textile Industry			
Alkaline Bemberg Rayon Process	Cu-P	PA-322	Present as cuproammonium salts.
Dyes	Cr-P	EN-146	
Rayon Wastes (General	Zn, 20-1,000	PA-322	
Textile Mills	Fe-P	PA-322	
Vulcanized Fiber	Zn, 100-300	PA-322	
18. Tire Manufacturing Industry			
Cooling Tower Blowdown	Cr, 0.1 Zn, 0.1	EN-154 EN-154	

NOTE: P = present, but levels not quantified.